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IONIZATION AND PHOTO-ELECTRIC PROPERTIES OF VAPORS OF ALKALI METALS.

By S. Herbert Anderson.

Introduction.

IT is a well-recognized fact that the photo-electric effect may give some definite information of the nature of radiation and of the distribution of energy in light waves. The importance of this phenomenon makes it very desirable to have reliable quantitative data of the relation between the wave-length of the incident light illuminating a metal and the positive potential acquired by the metal under such conditions. So far the results of different observers show great discrepancies. E. Ladenburg,[1] working in the region λ 2,700 to λ 2,000, obtained data, which, according to his interpretations, show that the relation is a linear one and a verification of Plank's theory of radiation which may be expressed by

$$P = \frac{k_1}{e} n,$$

where P is the potential, e the elementary electrical charge, k_1 a constant and n the frequency of the incident light. Hull,[2] working in the region λ 1,710 to λ 1,230 obtained data which he interprets in the same way, while Kunz,[3] working over a range of λ 5,000 to λ 2,000 obtained data which verify his theory of radiation,[4] which may be expressed by

$$P = \frac{k_2}{e} n^2.$$

[1] Phys. Zeits., VIII., p. 590, 1907.
[2] Am. Jr. of Sc., XXVIII., p. 251, 1909.
[3] Phys. Rev., XXXIII., p. 208, 1911.
[4] Phys. Rev., XXIX., p. 212, 1909.

That is, the potential which the illuminated metal acquires varies as the *square* of the frequency and *not* simply as the frequency. More recently Wright[1] has obtained curves for the relation between the wave-length and positive potential which differ both from the results of Ladenburg and Hull and of Kunz, and might indicate that the phenomenon is of a resonance nature which would be in accord with neither Plank's nor Kunz's theory.

Furthermore, the work of Millikan[2] and Wright (*l. c.*) shows that the magnitude of the photo-electric effect is largely determined by surface conditions. Gehrts[3] has shown that the reflection of electrons and secondary electrons may produce effects which amount to 40 or 50 per cent. of the original effects; and consequently the methods of investigation must be such as to avoid these. Hughes[4] has shown that metal surfaces procured by distillation of the metals *in vacuo* give a larger photo-electric potential than is obtained from polished surfaces which have not been treated to a glow discharge, and is much more stable and constant. The work of all these observers shows that the photo-electric effect is far from a simple one. The exact law cannot be known until all the factors entering in are known and understood.

In the physical laboratory of the University of Illinois considerable work has been done upon the photo-electric effect of alkali metals. The advantages of work with these metals are: (1) a clean surface can easily be obtained by distillation *in vacuo*, and (2) these metals give larger photo-electric currents than any other metals. In investigations carried on by Professor Kunz, Dr. J. G. Kemp and the author, it has been observed that there is present in tubes prepared as photo-electric cells, containing alkali metals, a conduction due to something else than the electron current arising from the photo-electric action. It was thought that possibly this was due to ionization of the vapor of the alkali metals. Therefore the following investigation was undertaken to determine (1) whether or not there was a spontaneous ionization of the vapors of alkali metals and (2) to determine the magnitude of the currents of conduction for different temperatures.

Füchtbauer[5] has made some investigation of the spontaneous ionization of sodium vapor at temperatures ranging from 190° C. to 330° C. In a later paper[6] he gives some results obtained with cæsium vapor, but in

[1] PHYS. REV., XXXIII., p. 43, 1911.
[2] PHYS. REV., XXXIV., p. 68, 1912.
[3] Ann. der Phys., 36, p. 995, 1911.
[4] Proc. Camb. Phil. Soc., XVI., p. 167.
[5] Phys. Zeits., 10, p. 374, 1909.
[6] Phys. Zeits., 12, p. 225, 1911.

an atmosphere of helium of 196 mm. pressure, which would render the results quite different from those obtained with cæsium vapor alone. The temperatures he used for cæsium were from 150° C. to 210° C. In the former paper he gives a curve of conduction in sodium vapor which has very little of the characteristic features of an ionization curve. In the latter paper curves are obtained which do approximate to ionization curves.

Fredenhagen[1] in an investigation on the electrons given off from sodium and potassium made some observations of the conductivity of the vapors of these metals. He heated the potassium vapor up to 420° and the sodium up to 500° and found no currents that were measurable with a galvanometer that gave a deflection of one millimeter for a current of 3.7×10^{-10} amperes. The tube used for this part of his work was of the same type used by the author (Fig. 1, *A*).

The investigations of Füchtbauer and Fredenhagen do not throw much light on the photo-electric phenomenon. One cannot tell whether the conductivity they obtained is due to the vapor alone or to particles given off from the metal which was present in the tube containing the electrodes. And it is especially desirable to know whether or not there is a spontaneous ionization at ordinary temperatures, 20° to 25° C.

Experimental Method.

Two types of tubes were used in this investigation. In the first, Fig. 1, *A*, the two electrodes *a* and *b* were of the same material, viz., nickel, and of the same dimensions. In the second, Fig. 2, one electrode, *b*, consisted of the alkali metal, potassium or cæsium; the other, *a*, was a disk of nickel.

In using the tube of the first type potassium was placed in bulb *c* (Fig. 1), and a series of measurements taken when the field was from *a* to *b*, and also for the field from *b* to *a*, for the temperatures 25°, 50°, and 100° with the tube in darkness. Then the potassium was poured into the main tube and lodged between the electrodes, but not in contact with either of them, and a series of measurements taken for 25°, 50°, 100° and 150° with the tube in darkness and also with a beam of light falling on the potassium, but not on the electrodes.

With the tube of the second type (Fig. 2) a series was taken with potassium for one electrode for 25°, 50°, 100° and 150° both "in darkness" and with the "potassium illuminated." The fourth series of measurements were taken with the tube of the second type and with cæsium for one electrode for temperatures of 25°, 40°, 70° and 100°.

[1] Phys. Zeits., 12, p. 398, 1911.

EXPERIMENTAL DETAILS.

Construction and Preparation of the Tubes.—Tube No. 1 (Fig. 1, *A*), consisted of a glass tube 16 cm. long, 3 cm. in diameter at the middle. The two electrodes were nickel disks 19 mm. in diameter and 2 mm. thick. The distance between the electrodes was 2 cm. Nickel was used for the electrodes because it probably contains less gas, especially oxygen, at ordinary temperatures and pressures than platinum or silver and does not tarnish very readily.

In tube No. 2, Fig. 2, the bulb was 4 cm. in diameter. The upper electrode was a nickel disk 19 mm. in diameter and 2 mm. thick. The lower electrode was potassium for one set of experiments and cæsium

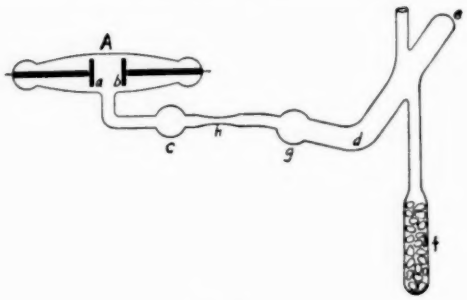

Fig. 1.

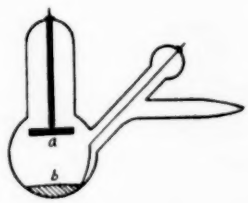

Fig. 2.

for another. The area of the potassium was about the same as that of the nickel electrode; and of the cæsium about 1 cm². The distance between the electrodes was 2 cm.

For the preparation of potassium the entire tube as shown in Fig. 1 was used. A piece of potassium was introduced into the tube through an opening at *e* and placed at *d*. The opening at *e* was then closed, and exhaustion by a Gaede pump begun. During the evacuation the tube *A*, containing the electrodes, was enclosed by a heating coil and kept at a temperature of 200° C. for about three hours, in order to remove as much as possible the gases occluded in the walls of the tube and in the electrodes, so that on subsequent heating gas would not be given off. The charcoal bulb *f* was heated to 300° or 400° during the exhaustion. When it was possible to pump the system down to a soft Röntgen ray vacuum with *A* and *f* still heated, then the heating coil was removed from *A* and the gas flame from under *f* and the exhusation carried to a hard Röntgen ray vacuum. The vacuum was tested by a discharge tube not shown in the diagram. The potassium was melted and the oily vapors from the crust pumped out during the melting. Potassium was then distilled into the bulb *g* in the following manner:

On carefully heating the potassium at *d* vapor went over into *g* and metallic potassium deposited on the walls of the bulb. The tube was then allowed to cool down and the process repeated. In this way sufficient potassium could be collected in *g*. The surface of the potassium obtained in this manner is as brilliant as polished silver. The whole system shown in Fig. 1 was sealed off from the pump, the potassium poured into bulb *c* and the charcoal bulb placed in liquid air. After waiting 20 or 30 minutes for the charcoal to absorb the remaining gas the tube *A* was sealed off from the rest of the system at *h*. By this method of preparing a tube as good a vacuum as possible is obtained.

The method of preparing tube No. 2, Fig. 2, was the same except that the potassium was poured into the tube and lodged at *b* before it was sealed off from the rest of the system.

A similar method was used in preparing tube No. 2 with cæsium for one electrode, but with the following modification: the tube (Fig. 1) was closed with a rubber stopper at *e* and exhausted. Then the whole system including the pump was filled with nitrogen at atmospheric pressure. A small bulb in which the metallic cæsium was contained was filled with nitrogen, the cæsium melted and poured into tube at *e*, which was then closed and exhaustion begun. From this point on the method of preparing the tube was the same.

Arrangement of Apparatus for Measuring Conductivity at Various Temperatures.—The method used for measuring the conductivity of the alkali vapor is shown diagrammatically in Fig. 3. The tube, either No. 1 or No. 2, was placed in the heating coil *H*, which was enclosed in a sheet-iron box *C*. This could be made light tight and the experiment was carried on in a dark room. The copper core of the coil and the sheet-iron box were both grounded. A wire from the electrode *a* passed through an insulating plug and was joined to a movable wire *W*, which made connection with a water rheostat *R*. To the water rheostat were connected the terminals of a storage battery B_1 of 1,800 volts and one terminal of the battery was grounded. From electrode *b* a wire passed through an insulating plug and was connected to one pair of quadrants of a Dolezalek electrometer. The other pair of quadrants was grounded.

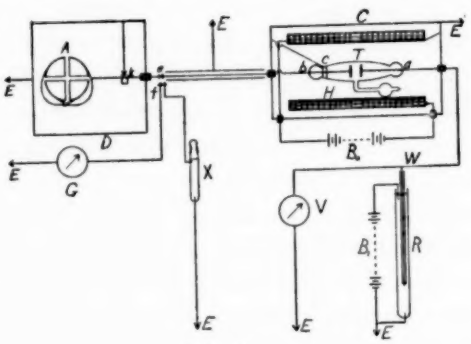

Fig. 3.

k is a plunger key by which the electrode b and the pair of quadrants to which it is connected may be grounded. c is a collar of metal foil placed around the tube near the end and connected to earth so that conduction over the outside of the tube may be avoided. The electrometer and connecting wires were enclosed in a sheet-iron box D, which was grounded.

The wire connecting electrode b to the electrometer was enclosed in a metal tube between C and D and this was also grounded. The scheme described above was used when the potential of electrode b was to be measured, and for measuring currents of the order 10^{-13} to 10^{-11} amperes. When currents of the order 10^{-11} to 10^{-9} were to be measured one terminal of a high resistance X was connected to the wire running from b to A at e. The other terminal of X was grounded. When k was opened a current flowed from b through X to the earth and the electrometer deflection gave the fall of potential across this resistance. And from these two quantities the current can be computed. When currents greater than 10^{-9} were to be measured the wire from b was disconnected from the electrometer at e and connected to a wire f from a galvanometer. The other terminal of the galvanometer was grounded.

The potential applied at a was measured by one of three electrostatic voltmeters V of the Kelvin and White type. Three voltmeters were necessary to cover the range required by the investigation; the first read from 0 to 90 volts, the second from 100 to 600, the third from 500 to 1,500.

When it was desired to pass a beam of light into the tube a slit in the box C was opened which was in line with the slit through the heating coil.

Heating Coil.—The tube was kept at a temperature higher than room temperature by means of a heating coil or electric furnace. The core of the furnace consisted of a copper cylinder 10 cm. in diameter and 25 cm. long. At the middle of the cylinder two slits were cut opposite to each other, 1.5 cm. by 0.5 cm., through which a beam of light could be directed into the tube placed inside the coil. The winding of the coil consisted of two layers of wire of the same number of turns so connected that the magnetic fields of the two layers were opposed. With this arrangement the magnetic force within the cylinder was found to be so slight as not to effect appreciably the movement of the ions in the tube.

Galvanometer.—The galvanometer used was a D'Arsonval instrument manufactured by W. G. Pye, Cambridge. The resistance was 122 ohms, and its period 9 seconds. The deflections were read by a telescope and scale at a distance of 2.5 meters. One millimeter deflection indicated a current of 0.837×10^{-9} amperes.

High Resistance.—The high resistance used was a liquid resistance, consisting of meta-xylol with a few drops of absolute alcohol. The

resistance could easily be changed by varying the proportion of meta-xylol and alcohol. The container consisted of a glass tube 0.9 cm. in diameter and 8.0 cm. long, with two platinum electrodes sealed through the glass 3.5 cm. apart. The tube was closed by a ground glass stopper. The resistance was observed to increase with the time probably due to evaporation of alcohol. But the resistance was constant for a period of a few hours required for a set of readings. The resistance used varied from 4.72×10^9 ohms to 14.3×10^{10} ohms.

Experimental Results.

Tube No. 1. Potassium in Bulb c.—The first series of measurements which will be presented were taken with tube No. 1 (Fig. 1, *A*), with the potassium in bulb *c* and with the tube in the dark. The method of taking the readings was as follows: The potential was applied at electrode *a* with the key *k* closed, so that the charge which would arise from electrostatic induction in electrode *b* and connecting wire would be removed through connection to earth at *k*. Potentials as high as 1,690 volts were applied. At 25°, 50° and 75° C. *nothing of the character of a regular conductivity was observed. But a phenomenon which has not been reported before was observed.* On opening the key *k*, after a *positive* potential was applied at *a* the electrometer gave a positive deflection which very soon came to a maximum. *Then there was a negative deflection which was nearly of a constant rate.* A test was made to determine whether this was due to a charge or a continuous current. With + 100 volts applied at *a* this movement of the electrometer needle toward the negative continued for three hours and fifty minutes, and the rate of deflection was nearly constant for the first fifty minutes. After the maximum negative deflection had been reached the electrometer needle drifted toward the zero at the rate of 0.5 mm. per minute, which was about the rate of the natural leak. So we would conclude that the effect is of the nature of a charge which at the temperature of 25° builds up very slowly and at first the rate of increase is a linear function of the time.

When a negative potential was applied the results were similar except that the directions of deflections were reversed. It was also observed that if a higher potential was applied after observations had been made for a given potential the "negative" current was not as large as was the case when a period of rest was given the tube with both electrodes grounded. Consequently it was found necessary in taking a set of readings to leave the tube earthed by both electrodes for 10 minutes between the measurement of the current for a given potential and the measurement for the next higher potential. Furthermore it was noticed

that if the tube was exposed to light while a potential was applied at *a*, there was a larger positive deflection and after the light was turned off the "negative" current was larger than before. After sufficient time in the dark the "negative" effect decreased to a constant value.

TABLE I.

"Positive" Charge and "Negative" Current at 25°.			"Positive" Charge and "Negative" Current at 50°.		
Potential in Volts.	"Positive" Charge.	"Negative" Current.	Potential in Volts.	"Positive" Charge.	"Negative" Current.
+ 100	+ 4.3	−0.4	+ 100	+ 2.5	− 6.2
300	12.0	1.2	300	6.5	16.2
500	19.8	2.0	500	14.0	24.8
700	25.7	2.8	700	18.0	36.0
900	35.5	3.5	900	20.5	47.0
1,100	44.4	4.5	1,100	25.0	58.0
1,300	—	—	1,300	28.0	72.0
1,490	off scale	5.5	1,490	32.0	110.7
1,690	" "	6.2	1,690	off scale	111.0
− 100	− 3.8	+0.47	− 100	− 2.5	+ 5.6
300	12.6	1.2	300	7.5	16.0
500	22.8	1.9	500	12.0	26.6
700	29.9	2.55	700	16.5	37.0
900	39.0	3.0	900	21.0	47.4
1,100	49.9	3.6	1,100	25.0	58.0
1,300	off scale	4.3	1,300	31.0	66.0
1,490	" "	5.0	1,490	31.5	84.0
1,690	" "	5.2	1,690	39.0	97.0

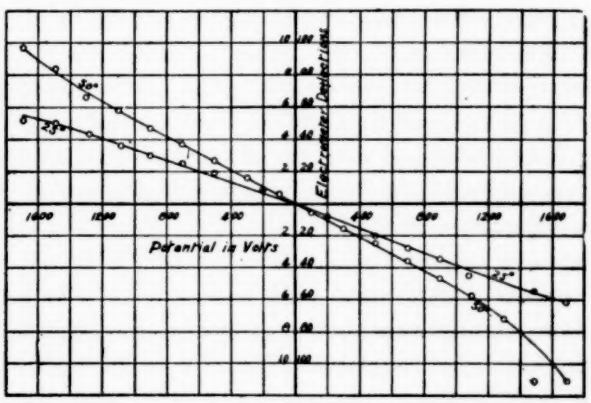

Fig. 4.

In Table I. there are given data which show the relation between the potential applied and the "positive" charge, that is, the first electrometer deflection after opening the key, which is in the same direction as the

field; and also the relation between the potential applied and the "negative" effect, which is a current appearing after the "positive" charge reaches a maximum and is in a direction *opposite* to the field. The "negative" current was measured by the rate of deflection of the electrometer. The "negative" current for 25° and 50° is shown by the curves of Fig. 4. For the curve for 50° the ordinates have 10 times the value that they have for the curve for 25°. *The remarkable feature of this phenomenon is that even with a potential difference of 1,700 volts there is a current in the opposite direction to what we would expect from our present knowledge of conductivity.*

When the tube was heated up to 75° the "positive" charge did not appear, but immediately on opening the key there was a "negative" deflection. The initial negative current was much larger than at lower temperatures, but the effect showed more the character of a charge in that it came to a maximum much sooner.

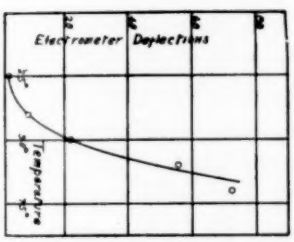

Fig. 5.

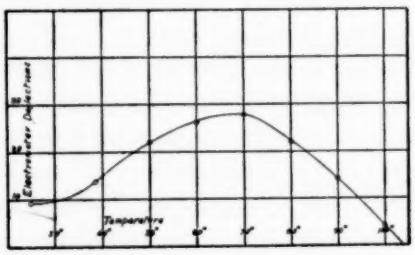

Fig. 6.

The variation of the initial "negative" current and of the charge with the temperature is shown by the curves of Figs. 5 and 6 respectively. In taking the readings for these curves a constant potential of + 400 volts was maintained. It was impossible to measure the currents for temperatures higher than 75° by this method. The "charge" curve, Fig. 6, shows that the effect reaches a maximum between 65° and 70°. If the curve is extended until it cuts the axis of abscissæ, it would appear that the effect disappears at about 104°.

At 100° when the potential was gradually increased up to + 700 volts a reversal of the electrometer deflection suddenly occurred and there was a *very large* positive deflection accompanied by a lighting up of the tube. There is then at this temperature and pressure a conductivity of the usual character through the vapor.

In order to determine whether or not this "negative" effect was due to anything else besides the potassium vapor, a new tube was made of the same form and dimensions in which no potassium was present. The

new tube was made with new electrodes and from new glass tubing thoroughly cleaned. The cocoanut charcoal used for exhaustion was freshly burned. The tube was pumped out with a new Gaede pump which had never been used for the exhaustion of tubes where alkali metals were present. The tube was pumped out to a hard Röntgen ray vacuum, the charcoal bulb immersed in liquid air for about 20 minutes and then the tube was sealed off. This tube showed the same "negative" effect as the one with potassium vapor. When first tried immediately after sealing off, it gave no positive deflection when a positive potential was applied, but a negative deflection the rate of which was about five times as great as that observed in the former case. After leaving in the dark and grounded by both electrodes for 10 hours there was then observed, when a positive potential was applied and the key opened, first a positive charge which was followed by a negative current which was smaller than the one observed when the tube was first tried. When a 16-candle-power incandescent lamp shone on the tube, the negative current increased and the positive charge entirely disappeared. After leaving in the dark for a few hours the positive charge reappeared and the negative current decreased. Hence it seems that this phenomenon (1) arises from the glass tube or the metal electrodes, (2) is affected by light, (3) is diminished by the presence of potassium vapor. Four tubes with similar electrodes of nickel and containing potassium vapor, one tube with nickel electrodes and no alkali vapor, and one tube with aluminum electrodes and no alkali vapor, *all showed the same phenomenon*.

No attempt is made at this time to explain this effect, but the observations made are presented and must be taken account of in measurements of small conductivities through gases.

Tube No. 1. Potassium between the Electrodes.—As the vapor of potassium shows no spontaneous ionization for the range of potentials and temperatures used, the next problem that presents itself is whether or not the potassium gives off particles which are carriers of electricity. For this investigation the potassion in bulb *c* was melted and poured into the main tube and lodged between the electrodes, but not in contact with either of them. Measurements were made of the currents for temperatures 25°, 50°, 100° and 150° with the tube in darkness and with the potassium illuminated by a beam of light. The source of light was a 16-candle-power incandescent carbon filament lamp, supplied from a storage battery of 120 volts. The beam of light did not fall on the nickel electrodes, though of course some reflected light did reach them. The results obtained are shown by the curves of Fig. 7. The curves with solid lines represent the currents with the "potassium in darkness," those

with broken lines represent the curves with the "potassium illuminated."

Attention is called to four particulars of these curves: (1) the "negative" effect persists for 25° and 50° in darkness and is the same order of magnitude as occurred when the potassium was in bulb *c*; this disappears for 100° in darkness and is not apparent for any of the temperatures tried

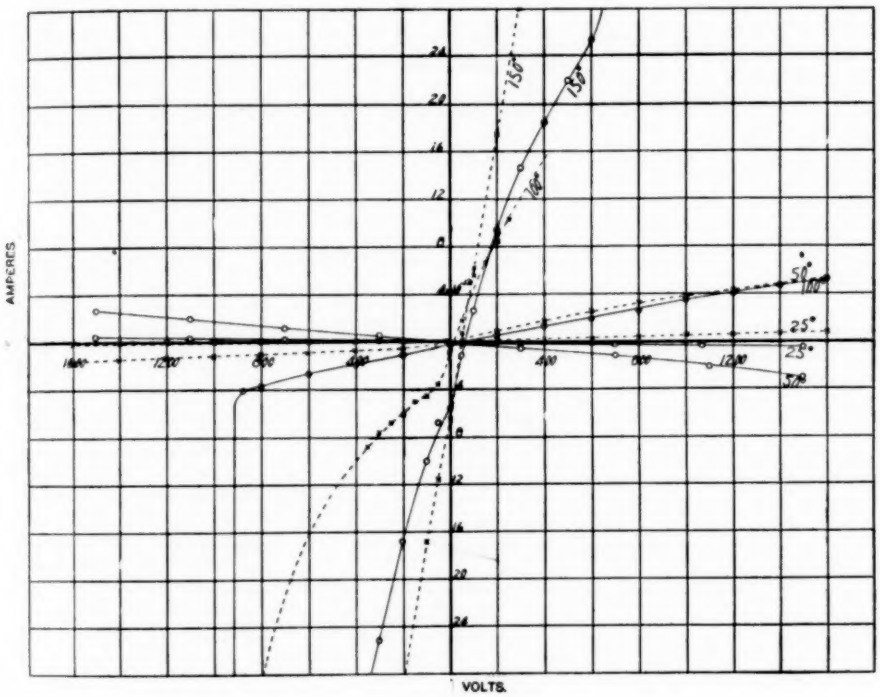

Fig. 7.

when the potassium is illuminated; (2) the linear character of the curve for 100° in darkness and the abrupt bend in the negative branch at 875 volts; (3) for 25°, 50° and 100°, "potassium illuminated," the positive branches of the curves show larger currents than the negative; (4) for 100° and 150° there is a negative current when no potential is applied. These peculiarities can be better explained later after the presentation of the phenomena of tube No. 2.

Tube No. 2. Potassium.—This tube gives more nearly than tube No. 1 the conditions that are realized in a photo-electric cell prepared for determining the maximum positive potentials assumed by a metal under the action of light. The conductivity was measured with the tube "in darkness" and with the "potassium illuminated" at the temperatures of 25°, 50°, 100° and 150°. The results are shown by the curves of Fig. 8.

The solid lines represent the currents with the "potassium in darkness," the broken lines the currents with the "potassium illuminated." For both of the curves for 150° the ordinates have 10 times the value marked on the figure, that is, the unit is 10^{-9} instead of 10^{-10}, which applies to the other curves.

One of the most interesting points brought out by this series of measurements is the existence of a negative current when no electric field is

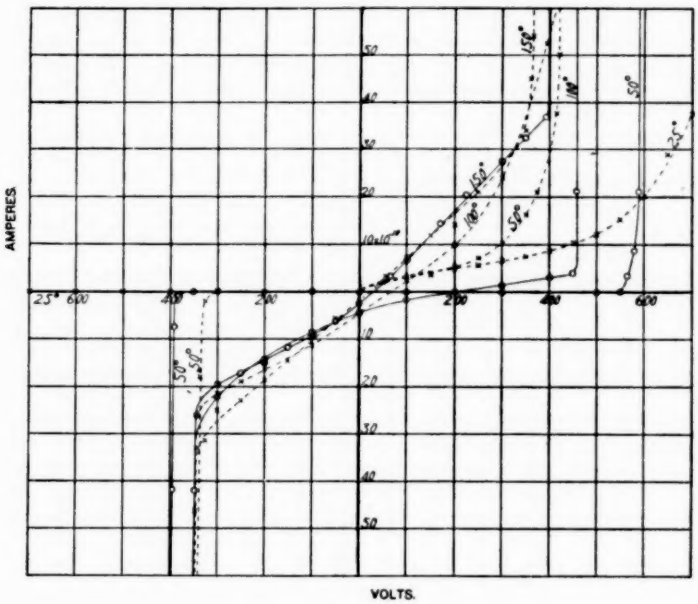

Fig. 8.

applied; that is, there is a positive current from b to a, Fig. 2, from the potassium electrode to the nickel electrode. This phenomenon was observed and has been investigated by J. W. Woodrow[1] in this laboratory. This effect is apparent at 25° in darkness and at 50°, 100° and 150° with the potassium illuminated as well as in darkness. Woodrow found this effect characteristic of the alkali metals. This effect for potassium and cæsium is shown by the curves of Figs. 9 and 10. The curves of Fig. 9 show how the negative charge on the potassium or cæsium increases with the time. In order to obtain the readings for these curves the alkali metal electrode, b, was connected to the electrometer and a was earthed. The curves of Fig. 10 show the increase of the current with the temperature. (The ordinates for the potassium curve have a larger value than for the cæsium curve.) These curves are introduced here because of

[1] PHYS. REV., XXXV., p. 203, 1912.

their bearing upon the author's results and as a confirmation of Woodrow's observations.

The second point of interest of this tube is that at 25° "in darkness," when a given potential is applied at *a*, the current occurring is not con-

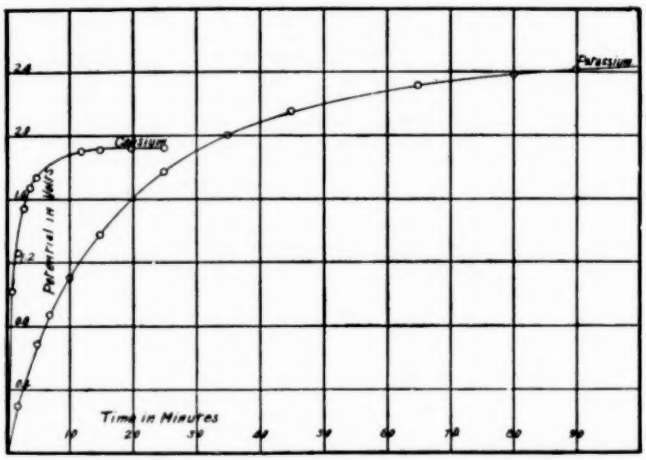

Fig. 9.

stant. This is shown by the curves of Fig. 11. Curve *B* shows how the current varies when + 300 volts is applied, and curve *B'* when − 300 volts is applied. *B'* could not be carried farther as the deflections went

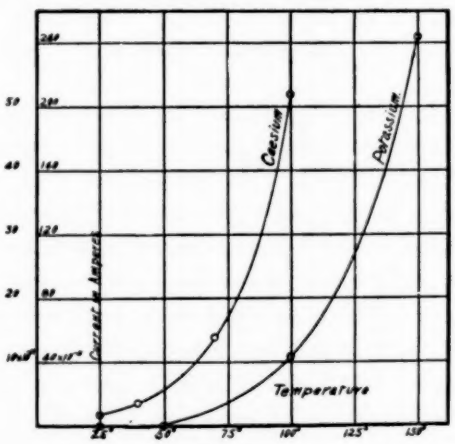

Fig. 10.

off the scale. When no potential is applied, that is, when *a* is grounded and *b* is connected to the electrometer the negative current, mentioned above, decreases as the charge on the electrode *b* builds up. This is shown

by curve A. When the ordinates of A are subtracted algebraically from those of B and B' two curves C and C' respectively are obtained which are almost identical, except that ordinates are of opposite sign. Hence it

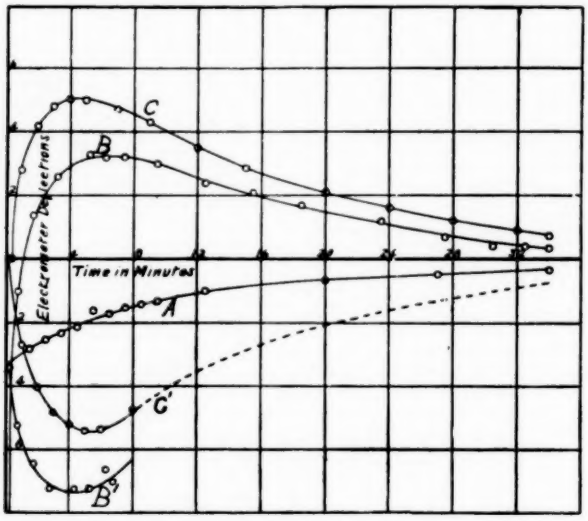

Fig. 11.

would appear that the difference between B and B' is due to the effect of A.

The equation of a curve of the type of C and C' is of the form

$$i = Ae^{-at} + Be^{-bt} + C.$$

The constants of this equation can be obtained by taking values of i for five different values of t and thus getting five equations with the five unknowns A, B, C, a, and b. The actual values of these constants are of no consequence as they will give us no further information of the nature of the phenomenon; so the determination of the constants was carried out only far enough to see that all five constants are real and different from zero. These curves then may be represented by an equation of this form. From this fact we may conclude that there are *three* distinct effects occurring in the tube in addition to the current of curve A: (1) a positive current which decreases according to the equation

$$i = Ae^{-at},$$

(2) a negative current decreasing according to

$$i = Be^{-bt},$$

(3) and a constant current given by

$$i = C.$$

TABLE II.

Tube No. 2, Cæsium.

Temperature 25°.

In Darkness.		Cæsium Illuminated.	
Potential in Volts.	Current in Amperes.	Potential in Volts.	Current in Amperes.
0	-1.83×10^{-12}	0	$+0.58\times10^{-11}$
+ 200	+ 1.502	+ 100	10.56
− 400	3.34	300	15.4
600	6.44	500	18.0
800	11.27	700	21.5
1,000	16.85	900	24.1
1,200	23.85	1,000	25.4
1,400	33.5	1,640	192.0
1,600	38.3		
1,650	40.2		
− 200	− 3.35	− 200	− 0.963
400	5.47	400	1.26
600	8.52	600	1.705
800	13.6	800	2.295
1,000	20.2	1,000	3.37
1,200	30.1	1,200	4.77
1,400	47.0	1,400	7.03
		1,600	11.5
		1,650	13.2

Temperature 40°.

0	-5.94×10^{-12}	0	$+0.222\times10^{-11}$
+ 100	2.58	+ 10	14.2
200	1.29	88	23.1
300	1.4	410	83.7
400	+ 6.87	500	543.0
500	16.8		
600	22.6		
625	60.2		
− 100	− 7.76	− 12	− 4.82
200	9.9	57	6.33
300	19.5	100	8.15
400	41.2	200	8.7
600	837.0	300	11.85
		366	25.6
		550	83.7
		600	234.0

TABLE II.—*Continued.*

Temperature 70°.

In Darkness.		Cæsium Illuminated.	
Potential in Volts.	Current in Amperes.	Potential in Volts.	Current in Amperes.
0	-14.0×10^{-10}	0	-0.036×10^{-10}
+ 100	1.2	+ 100	+ 1.88
200	+ 15.6	200	2.48
300	78.8	300	3.35
370	232.0	400	83.7
		500	167.5
− 100	− 0.293	− 100	− 0.547
200	0.58	197	2.53
300	1.7	300	14.2
321	2.53	400	25.05
420	217.0	500	201.0

Temperature 100°.

0	-0.5×10^{-10}	0	-0.248×10^{-10}
+ 100	+ 0.1	+ 100	1.43
200	0.9	190	2.68
300	2.64	300	12.55
400	10.05	400	20.05
500	23.4	500	38.2
600	134.0	600	41.8
665	655.0	800	100.5
		1,000	309.0
− 100	− 1.09	− 100	− 1.6
200	2.25	200	4.18
300	3.35	300	8.37
400	10.9	400	16.75
500	25.01	600	67.0
600	45.2	800	159.0
700	75.3	1,000	259.0
825	250.5		

Curves B and B' are typical of all those taken for various potentials. For negative potentials of 500 volts or more the initial current is positive; this decreases and is followed by a negative current which increases to a maximum and then decreases.

The features of the curves of Fig. 8 to which attention will be called later are: (1) with the "potassium illuminated" all the curves obtained when a positive potential was applied at a show the characteristics of ionization curves, though saturation is not clearly marked; (2) the negative branch of the curve for "potassium illuminated" at 25° shows practically no current; (3) the abrupt bend away from the axis of abscissæ

in all the curves obtained when a negative potential was applied; (4) the curves "in darkness" and "potassium illuminated" very nearly coincide for the negative branches of the curves at 100°, and for both the positive and negative branches of the curves at 150°.

Tube No. 2. Cæsium.—The observations in this series were carried out in the same manner as for tube No. 2, potassium, except that the temperatures used were 25°, 40°, 70° and 100°. The results are given in the data of Table II. No curves are shown because they differ in no essentials from those for potassium, Fig. 8. The following features are worth noting: (1) the existence of a negative current when no field is applied, as with the potassium, due to the emission of positive particles from the cæsium; (2) the great increase in the current at 25° and 40° when the cæsium was illuminated over the currents occurring when the cæsium was in darkness.

Discussion of Results.

The experiment with tube No. 1 with potassium alone between the electrodes, that is, with the solid potassium in bulb *c*, Fig. 1, shows that there is nothing of the character of a spontaneous ionization at a temperature as high as 75°. No conductivity of the usual type was observed when a potential of 1,700 volts was applied. At a temperature of 100° when the potential is gradually increased there is a luminous discharge at 700 volts. But there is no current before this occurs. The abruptness of the discharge indicates that there are no ions present until produced at this instant. At this temperature, 100°, the velocity of agitation is relatively large. Some molecules acquire sufficient velocity so that when a collision with another molecule occurs the electron system of the atom is put in such an unstable condition that the electric force due to the 700 volts difference of potential between the electrodes is sufficient to drag an electron from the atom and ionization occurs. The ions thus produced acquire sufficient velocity under the action of the electric field to produce ionization by collision and the luminous discharge occurs.

The absence of spontaneous ionization is further verified by the fact that when in tube No. 1 the potassium was introduced into the tube so as to lie between the electrodes no conductivity of the usual type occurred until the temperature was raised to 100°.

Woodrow found that the alkali metals in the dark gave off positive particles and that the current arising therefrom increased with the temperature according to the relation

$$i = aTe^{-b/t},$$

where a and b are constants and T the absolute temperature (see curves of Fig. 10). This will be used as a basis for explaining the peculiarities of the curves of Fig. 8, to which attention was called earlier.

The curve for 100° "in darkness" is a straight line up to 1,600 volts. It does not seem reasonable to assume that this is a portion of an ionization curve or saturation would be reached before 1,600 volts. Since positive particles are given off from the liquid potassium at this temperature in some considerable numbers, we may assume that from the surplus of electrons left in the metal some will be given off under the action of the field between the electrodes. When equilibrium is reached the same number of positive and negative particles will be given off and there will be a steady current. The number of particles given off will increase with the field and if the relation is a linear one the curve is explained. Since in all probability the positive ions are atoms of potassium, potassium will be deposited on electrode b. If this is the case the other peculiarities of the curves of Fig. 7 can be explained.

After this curve is taken with the positive potential the curve with the negative potential is taken at the same temperature. Now with the field in this opposite direction to what it was formerly positive particles will be given off from the layer of potassium on electrode b in addition to positive and negative particles given off from the potassium in the tube. The direction of the field will facilitate the natural tendency of the potassium to give off positive particles. This accounts for the fact that in the negative branch of the curve for 100° "in darkness" the currents are a little larger than in the positive branch. Furthermore at 875 volts there is an abrupt bend in the curve showing ionization by collision. At this potential the positive particles acquire sufficient velocity to ionize the vapor. And increase of ionization is very rapid when positive ions begin to produce ionization by collision.

For 150° the order of taking observations was the same as for 100° and this would result in a greater deposit of potassium on electrode b. The negative branch of the curve "in darkness" becomes parallel to the current axis for a lower potential than the positive branch. And this is accounted for by the fact that positive particles are given off from electrode b when the field is in this direction.

Attention has been called to the fact that for 25°, 50° and 100° the positive branches of the curves for "potassium illuminated" give larger values for the currents in the linear portions of the curve than do the negative branches. This can be explained also by assuming that there is some potassium deposited on b. For when the direction of the field is from a to b under the action of reflected light electrons will be given off,

while they will not be given off so readily when the field is from *b* to *a*.

The negative current at 100° and 150° with no field present may also be explained by the deposit of potassium on electrode *b*.

Of course this deposit of potassium on *b* is of no vital importance in the investigation, but the peculiarities of the curves of Fig. 7 are very reasonably explained by this fact.

Attention previously has been called to the fact that some of the curves of Fig. 8, taken with tube No. 2, potassium, show the characteristic features of ionization curves, viz., (1) a straight line where the current obeys Ohm's law, followed by a bending toward the axis of abscissæ, (2) a portion parallel to the axis of abscissæ where saturation occurs, (3) a rapid rise away from the axis of abscissæ where ionization by collision begins. The curves obtained differ from the ionization curve above described in that at no point does the curve become parallel to axis of abscissæ. This is due to the source of ions. In order to have a portion of the curve parallel to the axis of abscissæ, the source of ions must be such that the rate of producing these primary ions is constant. This is the case where the gas is ionized by Röntgen rays or a radioactive substance. In this experiment the source of the ions is the photo-electric action of the potassium, and the rate of production increases with the potential applied. This accounts for the straight line portion of the curve seen in the curves of Fig. 8. The point where the curve begins to bend away from the straight line corresponds to the potential where ionization by collision begins. In the curves taken at 100° and 150° the straight line portion of the curve is not so apparent because at these temperatures ionization by collision begins at a lower potential.

TABLE III.

In Darkness.

Temperature.	Current.				
	0 Volts.	100 Volts.	200 Volts.	300 Volts.	400 Volts.
25°	-0.0283×10^{-11}	− 0.035	− 0.055	− 0.071	− 0.101
50°	− 0.59	− 0.556	− 0.47	− 0.38	− 0.4
100°	− 44.0	− 22.0	− 1.56	+ 15.0	+30.0
150°	−244.0	+670.0	+1,780.0	+2,760.0	off scale.

Potassium Illuminated.

Temperature.	Current.				
	0 Volts.	100 Volts.	200 Volts.	300 Volts.	400 Volts.
25°	-0.075×10^{-10}	+ 3.2	+ 5.0	+ 6.5	+ 8.7
50°	− 0.242	+ 2.6	+ 5.0	+ 10.5	+ 28.5
100°	− 4.3	+ 2.3	+ 9.6	+ 23.8	+ 58.5
150°	−21.0	+70.0	+158.0	+250.0	+1,010.0

The curves taken with cæsium are similar to those with potassium.

The negative branch of the curve taken at 25° with the "potassium illuminated" shows practically no current of the same magnitude as the other curves. This is what would be expected; for with the field in that direction no electrons would be given off. Any current that occurs must be due to the positive particles. It is reasonable to expect that if a higher voltage had been applied there would have occurred an abrupt bend as in the curve for 50°. Such a bend occurs where the positive particles acquire sufficient velocity to produce ionization by collision.

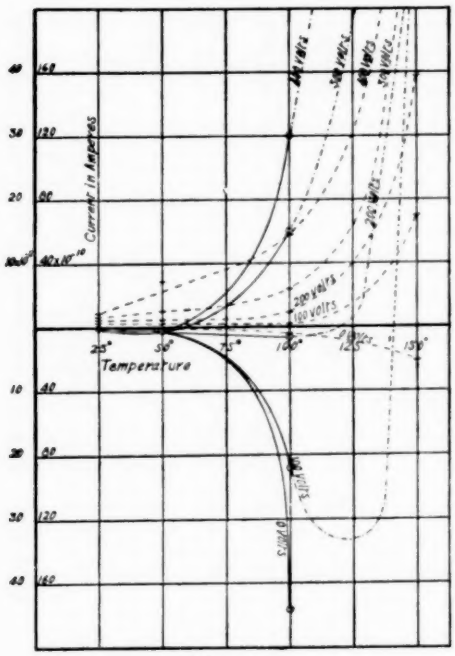

Fig. 12.

The close agreement of the curves for "in darkness" and "potassium illuminated" in the negative branches for 100° and 150° shows that the source of ions must be the positive particles whose expulsion from the potassium is independent of the action of light.

It is rather remarkable that for the curves for 50°, 100° and 150° the abrupt bend occurs at the same potential very nearly, 350 volts. This indicates that the velocity acquired to produce ionization by collision is due to the electrical field almost entirely and that the initial velocity for all temperatures is small compared to this.

In order to show how the currents obtained with tube No. 2, with electrode *b* of potassium vary with the temperature we may plot temperatures as abscissæ for a given potential. These curves are given in Fig. 12, and the data for them in Table III.

The solid lines represent currents measured with the potassium "in darkness." The portions of the curves represented by dots and dashes have been determined only in a qualitative way. Reference to the table will show that there is some warrant for drawing them as they are. The curves of broken lines represent the currents measured with the "potassium illuminated." The ordinates for the latter have 40 times the value of the former. For all these curves the field is from *a* to *b*, so that the

positive currents are due to electrons given off from the potassium or to ions produced by them, while the negative currents are due to the positive particles. The curves show that for temperatures up to 50° for the potassium in darkness the emission of positive particles is predominant for all potentials. But for higher temperatures the emission of electrons is predominant for potentials of 300 volts and more. It is quite likely that the critical temperature is the melting point of potassium, 62°.

If the curve for 0 potential, "potassium illuminated," were plotted on the same scale as the curve for 0 potential, "potassium in darkness," it would be seen that the two very nearly coincide, as the data of the table show. This means that the electron current due to the photo-electric effect is very small compared to the emission of positive particles from the potassium at higher temperatures. The greatest relative difference between the two effects is at 25°. At this temperature when the light is applied the current changes from a small negative value to a positive value 25 times greater. But for higher temperatures the resulting current is negative both with and without light and the difference between the two currents is only of a few per cent. However, when a field is applied from *a* to *b* then the electron current becomes predominant.

Quantitative Results.

Ratio of the Number of Electrons Given off to the Number of Atoms Present.—From the electron current occurring when the potassium is illuminated either with or without an applied potential, the number of electrons leaving wither with or without an applied potential, the number of electrons leaving the surface of the alkali metal per second can be computed and compared with the number of atoms in the active layer. At 25° the negative current for potassium in darkness with zero potential is 0.283×10^{-12} amperes. And the positive current when the potassium is illuminated is 7.5×10^{-12} amperes. Since the positive current must be the difference between the current due to the electrons and that due to the positive particles, the current of electrons must be

$$7.5 \times 10^{-12} + 0.283 \times 10^{-12} = 7.783 \times 10^{-12} \text{ amperes},$$
$$7.78 \times 10^{-12} \text{ amp.} = 7.78 \times 10^{-13} \text{ e.m. units.}$$

The number of electrons reaching the electrode per second is

$$\frac{7.78 \times 10^{-13}}{1.55 \times 10^{-20}} = 5.02 \times 10^{7},$$

where 1.55×10^{-20} is the value of e in electromagnetic units.

The potassium was in the shape of a disk with a very nearly flat surface and a radius of about 1 cm.

Area of potassium $= \pi 1^2 = 3.1416$ cm^2.
Diameter of potassium atom $= 4.74 \times 10^{-8}$ cm.
Cross-sectional area occupied by one potassium atom is

$$(4.74 \times 10^{-8})^2 = 2.25 \times 10^{-15} \text{ cm}^2.$$

$$\text{Number of atoms in one layer} = \frac{3.1416}{2.25 \times 10^{-15}} = 1.397 \times 10^{15}.$$

Ladenburg[1] has found that the thickness of the layer of metal effected by light is about 10^{-4} cm. Hence the number of layers of atoms of potassium in the active layer of the metal is given by

$$\frac{10^{-4}}{4.74 \times 10^{-8}} = 2.11 \times 10^{3}.$$

The total number of atoms in the active layer is

$$1.397 \times 10^{15} \times 2.11 \times 10^{3} = 2.95 \times 10^{18}.$$

Ratio of number of atoms to number of electrons given off per second is

$$\frac{2.95 \times 10^{18}}{5.02 \times 10^{7}} = 5.88 \times 10^{10}.$$

That is, one atom out of 5.88×10^{10} gives out one electron per second. At this rate it would require 5.88×10^{10} seconds or 1,860 years for each atom to give out one electron. Of course the electron current can be considerably increased by using a more intense light and one of shorter wave-length. And then the ratio between the number of atoms and the number of electrons given off will be much decreased. But this computation serves to emphasize the fact that the number of atoms effected is exceedingly small. This may be due to one of two causes, or possibly to both: (1) only a very few of the atoms are in condition to give out electrons under the influence of light; (2) light has a structure and the energy is not uniformly distributed over the light wave front, but is concentrated along certain lines as suggested by the theory of J. J. Thomson[2] and amplified by Kunz.[3] In this investigation there is some evidence in favor of the first explanation. A comparison of the curves for "potassium illuminated" and "in darkness" in Fig. 8 will show that as the temperature increases the effect of light on the current becomes less and less, until at 150° the curves for "potassium illuminated" and "in darkness" almost coincide. That is, at this temperature electrons are given off just as readily without light as with it when an electric field is applied, or the photo-electric action at this temperature is practically

[1] Ann. der Phys., 12, p. 558, 1903.
[2] Proc. of Camb. Phil. Soc., 14, pt. 4, p. 41, 1908.
[3] PHYS. REV., 29, p. 212, 1909.

zero. Hence it appears that the electron current depends more upon the condition of the metal than of the incident light. If the number of electrons given off depended alone on the structure of light, the electron current should be much larger with light than without light for all temperatures.

At 150° with + 100 volts potential the current is about 1,000 times larger than at 25° and with zero potential. But even with this current the ratio between the number of atoms and the number of electrons given off is a large one, 5.88×10^7. So that even at this temperature the number of atoms in condition to give off electrons is small.

Estimate of the Maximum Vapor Pressure Possible of Potassium.— When light is incident on a metal the electrons are given off with a velocity which can be obtained by the relation

$$Pe = \tfrac{1}{2}mv^2,$$

where e is the charge of the electron and P the maximum positive potential assumed by the metal in the photo-electric action. The maximum velocity of the electrons from potassium in this work when zero potential was applied is due to the shortest wave-length of visible light, about λ 4,200. D. W. Cornelius in this laboratory found the velocity due to this wave-length to be 6.21×10^7 cm. per second. When there is an electric field acting the velocity of the electrons increases beyond the initial velocity until the electron has sufficient velocity to produce an ion by collision. This relation is expressed by

$$W = Eel + \tfrac{1}{2}mv^2,$$

where W is the energy required to produce an ion, E the electric field, e the elementary electrical charge, m the mass of the electron, v the initial velocity and l the distance from the surface of the metal that the electron must go to gain sufficient velocity to produce ionization. The value of E can be taken from the curve at the point of departure from a straight line. From the curve for 25°, Fig. 8, we find the potential corresponding to this point of departure to be 350 volts. As the electrodes were 2 cm. apart, the value of E is

$$\frac{350}{2} = 175 \text{ volts per cm.},$$

$$E = \frac{175}{300} = 0.583 \text{ e.s. units per cm.},$$

$$e = 4.65 \times 10^{-10},$$

$$m = 8.7 \times 10^{-28},$$

$$v = 6.21 \times 10^7.$$

The value of W is taken at 1.58×10^{-11} ergs, which is the value obtained by Bishop[1] for hydrogen and also by Kemp in this laboratory. So far as has been investigated this value does not vary very much for different gases, so it will be assumed that it is a reasonable value for potassium vapor.

$$l = \frac{W - mv^2/2}{Ee} = \frac{1.58 \times 10^{-11} - \frac{8.7 \times 10^{-28}(6.21 \times 10^7)^2}{2}}{5.83 \times 10^{-1} \times 4.65 \times 10^{-10}}$$

$$= \frac{1.58 \times 10^{-11} - 0.169 \times 10^{-11}}{2.71 \times 10^{-10}}$$

$$= 5.2 \times 10^{-2} \text{ cm.}$$

Now the mean free path of the molecules of potassium vapor must be at least this great or there could be no ionization by collision at this field strength. Assuming this to be the minimum mean free path we can calculate the maximum number of molecules per cm^3. The mean free path is given by

$$l = \frac{1}{\sqrt{2}\pi n \sigma^2},$$

where n is the number of molecules per cubic centimeter and σ is the diameter of the molecule. We have then

$$n = \frac{1}{\sqrt{2}\pi l \sigma^2} = \frac{1}{\sqrt{2}\pi 5.2 \times 10^{-2}(4.74 \times 10^{-8})^2}$$

$$= 1.925 \times 10^{15}.$$

We may assume that at the temperature and pressure existing in the tube the potassium vapor acts as a perfect gas and so compute the pressure from

$$P = \frac{P_0 T n}{T_0 n_0},$$

where $P_0 = 760$ mm. pressure, $T_0 = 273°$, n_0 the number of molecules in a cubic centimeter of gas at standard conditions and is equal to 2.72×10^{19}, T the absolute temperature of the vapor and n the number of molecules of the vapor per cubic centimeter. Hence

$$P = \frac{760 \times 298 \times 1.925 \times 10^{15}}{273 \times 2.72 \times 10^{19}}$$

$$= 0.0587 \text{ mm.}$$

[1] PHYS. REV., 33, p. 325, 1911.

This is of the order of magnitude that would be expected. The only other determination made of the vapor pressure of potassium is one by Keyes[1] from theoretical considerations for 400° which he gives as 1.4 mm.

This problem of conductivity in alkali vapors is by no means solved. One very important feature which should be investigated is the effect of ultraviolet light. Does ultraviolet light ionize the vapor? And is there ionization from the electrons given off from the metal? From the data obtained some prediction can be made on this last point. Taking the energy necessary to produce an ion to be 1.58×10^{-11} ergs we can compute the velocity that an electron should have to produce ions by collision.

$$W = \tfrac{1}{2}mv^2,$$

$$v^2 = \frac{2W}{m} = \frac{2 \times 1.58 \times 10^{-11}}{8.7 \times 10^{-28}} = 3.63 \times 10^{16},$$

$$v = 1.9 \times 10^8 \text{ cm. per second.}$$

If we assume that the velocity of the electrons in the photo-electric effect varies inversely as the wave-length, we have

$$v_2 = v_1 \frac{\lambda_1}{\lambda_2}.$$

Taking $v_1 = 6.21 \times 10^7$ for $\lambda_1 = 4{,}200$ and $\lambda_2 = 2{,}000$, which is about the shortest wave-length which can be obtained with a quartz spectrometer, we find

$$v_2 = 6.21 \times 10^7 \frac{4200}{2000}$$

$$= 1.304 \times 10^8.$$

This is less than the value 1.9×10^8 computed above. But it is of the same order of magnitude and if the minimum energy to produce an ion is less than 1.58×10^{-11} ergs, it is entirely possible for the electrons set free from potassium by the action of the short wave-lengths of ultraviolet light to produce ionization by collision.

In some other work carried on by the author a potential of 5.85 volts was obtained from potassium illuminated by λ 2,100. This gives a velocity of 1.445×10^8 cm. per second which is some nearer the critical velocity to produce ionization.

These values would indicate that it would be well worth while to investigate this point.

[1] Jour. Am. Chem. Soc., XXXIV., p. 779.

SUMMARY.

1. This investigation has shown that when potassium vapor alone is between the electrodes of a tube there is no conductivity of the usual type at 25° and 50°; at 100° with a potential of 700 volts there is a current arising from ionization by the electric field. *Hence there is nothing of the character of a spontaneous ionization.*

2. When potassium was present in the tube but not in contact with the electrodes there is no conductivity of the usual type at 25° and 50°. At 100° there is a current due to particles given off from the potassium.

3. In a tube with two similar electrodes exhausted to the best degree possible there is a current of the order 10^{-13} amperes in a direction *opposite* to the electric field, which increases with the field. This phenomenon is effected by light and is decreased by the presence of potassium vapor.

4. The conductivity in potassium vapor when one electrode is potassium has been measured for temperatures up to 150°.

5. The conductivity in cæsium vapor when one electrode is cæsium has been measured for temperatures up to 100°.

6. Woodrow's observations on the emission of positive particles from alkali metals have been confirmed and for temperatures above 50° found to be large compared to the electron current.

7. The ratio between the number of electrons given off per second and the number of atoms present has been found for a given source of light to be $\frac{1}{5.88 \times 10^{10}}$.

8. At 150° light has practically no effect on the emission of electrons from potassium.

9. By comparing the currents for different temperatures in tube No. 2, with potassium electrode, it is found that the greatest relative effect of light on the emission of electrons is at 25°.

10. The maximum vapor pressure possible for potassium at 25° has been found to be 0.0587 mm.

The author wishes to express his indebtedness to Professor A. P. Carman and the department of physics for the facilities for this investigation, and to Professor Jakob Kunz who suggested the problem and has given many valuable suggestions.

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May, 1912.

HEATS OF DILUTION.

By William Francis Magie.

1. *Formulas for Heats of Dilution.*—Consider a system consisting of a solution made up by dissolving one gram-molecule of a salt in N gram-molecules of water and an additional mass of water. It is known that if the solution is diluted by the transfer of some of the water to it the heat capacity of the system diminishes. It is also known that the rate at which heat is evolved as the volume of the solution is thus increased (the heat of dilution) differs remarkably at different temperatures. These effects are connected by the formula

$$\frac{dl}{d\theta} = -\frac{dH}{dv}, \qquad (a)$$

in which l represents the heat of dilution, taken positive when heat has to be removed from the solution to keep its temperature constant as dilution proceeds, H, the heat capacity of the system, θ, the absolute temperature, and v, the volume of the solution. The proof of this formula is obtained by equating the quantities of heat which enter the system when it is transferred from an initial state at a certain temperature θ, to a final state at a slightly higher temperature $\theta + d\theta$, in two ways: (1) by raising the temperature of the system from the initial to the final value and then transferring the volume dv from the water to the solution at the final temperature; (2) by transferring the volume dv from the water to the solution at the initial temperature and then raising the temperature of the system from the initial to the final value; on the assumption that the external work done by the changes of volume which accompany dilution may be neglected.[1]

The experiments of Teudt[2] have shown that dH/dv is independent of the temperature, within the range of temperature open to experiment. Representing dH/dv by a, a function of the volume but not of the temperature, and integrating over a finite temperature range we have

$$l_2 - l_1 = -a(\theta_2 - \theta_1) \qquad (b)$$

or generally

$$l = -a\theta + e, \qquad (c)$$

where e is a function of the volume but not of the temperature.

[1] Thomsen, Thermodynamische Untersuchungen, Vol. 1, p. 65.

[2] Inaug. Diss. Erlangen: Beiblätter. XXIV., p. 1104 (1900).

The heats of dilution are determined by starting with an initial concentration of the solution and measuring the amounts of heat, L_v, evolved as the solution is diluted by the transfer to it of the volume v of water (practically by the increase of the volume of the solution by v). If the values of L thus obtained are plotted against the values of v and a curve drawn through the points thus given, the tangent to this curve at any point is the value of l for the corresponding concentration.

We may thus write formula (b) in the form

$$\frac{dL}{dv_2} - \frac{dL}{dv_1} = -\frac{dH}{dv}(\theta_2 - \theta_1) \qquad (d)$$

and integrate it with respect to the volume, since the changes of temperature caused by dilution are so small as not to affect the values of L found in the experiments. We obtain

$$(L_v - L_0)_2 - (L_v - L_0)_1 = -(H_v - H_0)(\theta_2 - \theta_1), \qquad (e)$$

in which the subscripts v and 0 refer to the final and initial concentrations.

It is more convenient to plot the curves and to express the formulas in terms of the concentrations than in terms of the volumes. This can be done when the concentration is defined in any arbitrary way, for the concentration c is practically independent of the temperature, so that we may write formula (d) in the form

$$\left(\frac{dL}{dc_2} - \frac{dL}{dc_1}\right)\frac{dc}{dv} = -\frac{dH}{dc}\cdot\frac{dc}{dv}(\theta_2 - \theta_1)$$

and setting $dL/dc = \lambda$, $dH/dc = \alpha$, we have

$$\lambda_2 - \lambda_1 = -\alpha(\theta_2 - \theta_1) \qquad (f)$$

and similarly

$$\lambda = -\alpha\theta + \epsilon. \qquad (g)$$

The dc/dv disappears from the formulas and we can define c as we please. In the experiments which are to be described c was set equal to $100/N$, where N is the number of gram-molecules of water containing one gram-molecule of the salt. The quantities α and ϵ are functions of the concentration but not of the temperature.

2. *Method of Observation.*—The experiments of Thomsen,[1] from which he concluded that the temperature coefficient of the heat of dilution is always positive, do not afford a demonstration that the foregoing formulas are valid. Since their validity depends upon the assumption that the

[1] Therm. Unters., Vol. 1, p. 80.

quantities a or α are independent of the temperature, an experimental verification of them will confirm this assumption. I have undertaken to obtain heats of dilution at different temperatures for solutions of certain salts for which the heat capacities were accurately known. The confirmation of the formulas is still not altogether satisfactory, but I am convinced that this is due to the experimental inaccuracies of the method employed.

The solution to be diluted was held in a silver calorimeter vessel, with a capacity of over 1,200 c.c. Usually so much of the solution was taken that the water contained in it weighed 500 grs. This was diluted with 500 grs. of water, run in from another silver vessel, after the initial temperatures of the solution and of the water had been determined. The thermometers used were made by Fuess, and were divided directly to fiftieths of a degree, so that they could be read by estimation to thousandths of a degree. It generally happened that neither the initial nor the final temperatures found were fixed, but changed progressively and quite uniformly as the liquids were stirred. In all cases several readings were made at intervals of a minute and an estimate was made, from the readings at the ends of the series and the rate of change of temperature determined, of the temperatures of the liquids, just before and just after mixing.

Trials with water in both vessels and the observations to determine the water equivalent of the vessel in which the liquids were mixed showed that the percentage error of the observations made in this way was not important when the changes of the temperature caused by the dilution was considerable, but the uncertainty of the measurements when the changes were of only a few thousandths of a degree, as was often the case with the more dilute solutions, was so great that the results for these cases are not reliable.

3. *Results.*—The results obtained are contained in the following table. The salts used were the chlorides of sodium, potassium, ammonium, barium, and strontium. The initial solution contained 25 gram-molecules of water to each gram-molecule or each half gram-molecule of salt as indicated in the tables. The initial concentration, on the convention adopted that $c = 100/N$, is therefore 4. In the first column of each table are given the concentrations reached by dilution from this initial concentration. In the other columns, under the values of the temperatures at which the experiments were carried out, are given the amounts of heat in gram-calories evolved (+) or absorbed (−) on the dilution from the initial to the indicated concentration of a solution containing one gram-molecule of the salt.

c	NaCl.		KCl.		NH_4Cl.	
	26.4°	16.8°	21°	3°	22.3°	3.7°
2	−157	−218	−165	−288	−20	− 94
1	−239	−335	−248	−460	−20	−145
½	−267	−379	−285	−555	−11	−169

c	$\frac{1}{2}BaCl_2$.			$\frac{1}{2}SrCl_2$.		
	24.5°	16.1°	7.1°	23.3°	16°	4.3°
2	+ 7	−42	−109	+ 35	− 3.4	− 75
1	+26	−51	−158	+ 66	+ 0.8	−117
½	+50	−39	−173	+102	+22.5	−144
¼	+85		−164	+134		−122

4. *Test of Integral Formula.*—The degree to which these results conform to formula (*e*) may be shown by one or two examples. The L_0 of the formula equals 0, and the two terms on the left are the numbers given for two temperatures for the same final concentration. The values of H are obtained fron the tables in my paper on the Specific Heat of Solutions, V.,[1] using the calculated rather than the observed results, and obtaining the initial value, when it is wanting, by interpolation. It is to be observed that the H of these tables is the heat capacity of the solution only and does not include that of the water needed to complete the system of which the H of formula (*e*) is the heat capacity.

In the case of sodium chloride we find that the successive values of $\frac{(L_v - L_0)_2 - (L_v - L_0)_1}{\theta_2 - \theta_1}$ are 6.3, 10, and 11.7, while starting with 448.2 for the heat capacity of a solution of sodium chloride for which $N = 25$, obtained by interpolation, we have for $-(H_v - H_0)$ the corresponding numbers 6, 10.2, 13.8. In the case of barium chloride we find for the successive ratios, using the extreme temperatures, the values 6.6, 10.5, 12.8, 14.3, while starting with 430.6 for the heat capacity of a solution for which $N = 25$, obtained by extrapolation, we have for $-(H_v - H_0)$ the corresponding numbers 6.2, 10, 13.7, 16.6. The results for the other substances show about the same sort of agreement, except in the case of ammonium chloride, in which there seems to be some systematic error.

5. *Test of Differential Formula.*—When the total heats of dilution (L) given in the tables are plotted against the corresponding concentrations (c), and the heat capacities (H) are plotted against the same concentrations, the tangents to the curves thus determined for the concentration furnish values of λ and α respectively. These values conform to the

[1] This REVIEW, Vol. XXV., p. 171 (1907).

relation expressed in formula (*f*). In all cases at the low temperatures, and in some cases at the higher temperatures, the *Lc* curve is nearly a straight line, as has been shown by Bishop[1] for solutions of KCl and of other salts at 25°. Since the values of α are never constant for all concentrations the *Lc* curve is really straight only by exception.

The curves for solutions of barium chloride furnish an illustration of the general form of these curves (Fig. 1). The tangent at concentration 1 to the curve for 24.5° is − 37; that to the curve for 7.1° is + 38. The difference of these tangents divided by the difference of the temperatures is − 4.3, and this is equal to the negative value of the tangent at the same concentration to the curve of heat capacities, as it should be to conform to formula (*f*). By calculation from these data we find that for the same concentration the temperature at which $\lambda = 0$ is 16°. The curve for 16° confirms this conclusion. A similar transition of λ from negative to positive values was found at 16° for concentration 2 in the case of strontium chloride, and at 22.3° for concentration 1.5 in the case of ammonium chloride. All these relations confirm the experimental results of Teudt, according to which the quantities *a* and α are independent of the temperature.

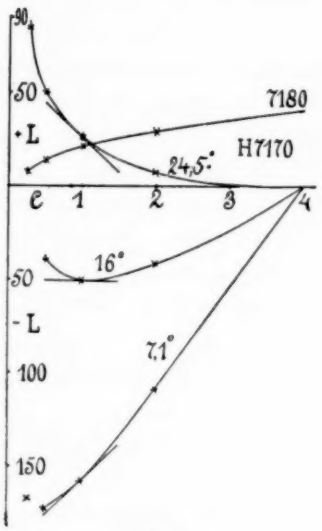

Fig. 1.

6. *Explanation of Heats of Dilution on the Association Theory of Solutions.*—The most striking thing about these heats of dilution is their very large proportionate change with change of temperature. The reason for this will be seen on an examination of formula (*c*). This formula shows that the heat of dilution is the sum of two terms of opposite sign, one of which is proportional to the absolute temperature, the other, independent of the temperature. The term $-a\theta$ is always positive, for the heat capacity of the system diminishes as the volume of the solution increases, so that *a* is negative. It corresponds to an evolution of heat. The other term *e* is negative and corresponds to an absorption of heat. These terms are both large and a change in one of them, proportional to the change in the absolute temperature, may result in a change in the difference between them which is large in comparison with that difference.

[1] This REVIEW, Vol. XXVI., p. 169 (1908).

The evolution of heat to which the term $-a\theta$ corresponds can be explained by considering the change in the number of degrees of freedom in the solution which results from dilution. It has been shown[1] that the rate of change of heat capacity represented by the factor a is proportional to the rate of change of dissociation, and that there must be some interaction between the molecules and ions of the solute and the molecules of water which brings about a diminution in the number of degrees of freedom of the water. I have used the word "interaction" instead of the less general word "association," which was used in the paper referred to, in deference to a suggestion made by Professor G. N. Lewis, at the Cambridge meeting of the American Physical Society, that the effect might be produced by changes in the state of aggregation of the molecules of water without there being any immediate association between the aggregations of water molecules and the solute. For the purpose of the present explanation it is a matter of indifference which view is taken. A study of the constants of the formula which represents the heat capacity of a solution shows that usually the number of degrees of freedom of the undissociated molecules of the solute and of the water affected by them is increased by solution, and that always the number of degrees of freedom of the ions and of the water affected by them is decreased. As dilution proceeds, therefore, and the molecules of the solution break up into ions, the number of degrees of freedom of the solution diminishes both by the removal of molecules from the solution and by the introduction of new ions. The change in the number of degrees of freedom is proportional to the change in the amount of dissociation. The energy which has been associated with the degrees of freedom thus removed from the solution is released in the solution and appears in the form of heat.

At the temperatures at which the experiments have been made and at which the formula (c) is valid, the energy associated with a degree of freedom is proportional to the absolute temperature. An evolution of heat proportional to the change in dissociation and to the absolute temperature is thus accounted for.

The heat absorbed, to which the negative term e corresponds, is nearly equal in amount at all concentrations to the heat evolved. It also is thus approximately proportional to the rate of change of dissociation. It may involve the heat of dissociation, corresponding to the work done in splitting up the molecules into ions. It may also involve the heat developed by the internal work done as the dilution proceeds and the volume of the system diminishes. Neither of these effects would depend

[1] Magie, "Specific Heat of Solutions," V., this REVIEW, Vol. XXV., p. 171 (1907).

primarily upon the temperature. The values obtained from the values of e for the heat absorbed at a given concentration by the complete dissociation of a gram-molecule of the salt are of the same order of magnitude as the heat evolved by combination of the atoms to form a gram-molecule of the salt. Thus in the case of sodium chloride the values of the heat absorbed by the complete dissociation of a gram-molecule at concentrations 2, 1, ½ are 22,700, 21,800, 21,200 gram-calories respectively. The heat of combination of a gram-molecule of sodium chloride is given in the Smithsonian Physical Tables as 97,000 gram-calories. By calculating from the heat absorbed by the dilution of a solution of potassium chloride from concentration 4 to concentration 2 we find the heat absorbed by the complete dissociation of a gram-molecule equal to 40,000 gram-calories, while the heat of combination of a gram-molecule of potassium chloride is 105,000 gram-calories. It seems reasonable to conclude that the term e of the formula contains, as an important part of it, the heat of dissociation.

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THE RELATION OF OSMOTIC PRESSURE TO TEMPERATURE.

BY WILLIAM FRANCIS MAGIE.

1. *Formula for Osmotic Pressure.*—By a thermodynamic argument[1] it is easy to establish the formula,

$$\frac{d^2p}{d\theta^2} = \frac{a}{\theta}, \qquad (a)$$

in which p represents the osmotic pressure, θ, the absolute temperature, and a, the rate at which the heat capacity of a solution changes as its volume increases. We shall consider the quantity a independent of the temperature (*vide* paper on Heats of Dilution in the present number of this REVIEW). Integrating on this assumption we obtain

$$p = a\theta(\log \theta - 1) + b\theta + e, \qquad (b)$$

in which b and e are quantities which are functions of the concentration of the solution, but are independent of the temperature. This formula expresses the proposed relation of the osmotic pressure to the temperature.

2. *Deduction of Formula for Heat of Dilution.*—When a solution is diluted by the addition of the small volume w of solvent, the heat which must be abstracted to keep the temperature constant is the measure of the change of internal energy E brought about by dilution, since the external work done in consequence of the change of volume is so small as to be negligible. This heat, which is proportional to the heat of dilution, is reckoned positive if the change in the internal energy is negative. The change of internal energy is expressed in terms of the change of free energy F by the formula

$$E = F - \theta\frac{dF}{d\theta}.$$

The change of free energy is measured by the work $-pw$ done by the osmotic pressure p when the original state of the solution and solvent is restored by separating the volume w of solvent from the solution in a reversible way by the use of a semi-permeable membrane. Setting $F = -pw$ and using the formula (b) we obtain

$$E = w(a\theta - e).$$

[1] Magie, The Specific Heat of Solutions, this REVIEW, Vol. IX., p. 65 (1899).

The negative value of E/w represents the heat of dilution l. We thus obtain the formula for the heat of dilution

$$l = -a\theta + e \qquad (c)$$

which was obtained in the paper referred to from other considerations.

3. *Test of Formula for Osmotic Pressure.*—The quantity a is known from observations of the heat capacity, the quantity e can be calculated from observations of the heat of dilution, and then the quantity b calculated from observations of the osmotic pressure or of other properties of solutions which depend on the osmotic pressure. The observations which are best adapted to furnish useful values of p and therefore of b are those of the freezing points and the boiling points of the solutions.

The only solutions for which I have been able to obtain the requisite data to test the formula are those of sodium chloride in water. The observations of Thomsen[1] furnish the heat capacities, those of Kahlenberg[2] the freezing and boiling points, and my own observations[3] the heats of dilution. In effecting the calculations it is convenient to express the quantity a in gram-calories per cubic centimeter, instead of in mechanical units. The osmotic pressure p is reduced to a consistent unit by dividing its value in dynes per square centimeter by Joule's equivalent. From the freezing points for sodium chloride solutions given in Kahlenberg's table (*l. c.*, p. 353) the corresponding osmotic pressures were calculated. They were then plotted against the number N of gram-molecules of water which contained one gram-molecule of salt in each case and a curve drawn through the points thus determined from which the osmotic pressure at 0° C. and at the standard concentrations could be read off. A similar calculation from the boiling points given in Kahlenberg's table (Series 3) (*l. c.*, p. 362), which furnished the largest number of available observations made at one time, established another curve for the determination of osmotic pressure at 100° C.

The necessary values of a are obtained from the tangents to the curve of heat capacities plotted against the concentrations, as described in my paper on "Heats of Dilution," by multiplying these tangents by the reduction factor $100/18N^2$. This factor is the value of dc/dv on the conventions that $c = 100/N$ and that $v = 18N$, which is sufficiently accurate at all concentrations, in view of the uncertainties in the observations. The values of l are obtained from the tangents to the curve of heats of dilution plotted against the concentrations, as described in the paper just referred to, by the use of the same reduction factor.

[1] Magie, "Specific Heats of Solutions," V., this REVIEW, Vol. XXV., p. 171 (1907).

[2] Jour. Phys. Chem., Vol. V., p. 339.

[3] "Heats of Dilution," this REVIEW, the present number.

The following table contains the values adopted for the concentrations 2, 1, ½, of a, of p_0 at the freezing point, and of l at 26.4° C., and the values calculated from them of the quantities b and e and of p_{100} at the boiling point.

c	a	p_0	l	b	e	p_{100}
2	0.00733	1.105	−0.1820	0.04656	−2.378	1.532
1	0.002833	0.550	−0.0361	0.01831	−0.8843	0.749
½	0.001139	0.280	−0.00332	0.007537	−0.3443	0.377

The values calculated for the osmotic pressures at the boiling point lie very exactly on the curve plotted from Kahlenberg's observations of the boiling points. They therefore furnish a satisfactory confirmation of the formula connecting the osmotic pressure with the temperature and thus incidentally confirm the assumption that the quantity a is independent of the temperature.

From the values adopted for a and e we find that the transition temperatures at which l passes from negative to positive values should be 51°, 39°, 29° C. for the concentrations 2, 1, ½ respectively.

4. *Test by von Babo's Law.*—Another test of the formula is obtained by calculating from it the ratio of the vapor pressure over water to the vapor pressure over a solution of a chosen concentration at different temperatures. According to von Babo's law this ratio should be independent of the temperatures. The ratios calculated for a sodium chloride solution of concentration 1 for temperature intervals of 20°, beginning with the freezing point and ending with the boiling point, are 1.01831, 1.01852, 1.01847, 1.01851, 1.01849, 1.01825. The ratio comes out appreciably constant. The observations of Emden[1] on solutions of sodium chloride are in accord with this result.[2]

The vapor pressures of solutions should conform to von Babo's law when the osmotic pressure obeys Gay-Lussac's law, that is, when the osmotic pressure is proportional to the absolute temperature. The following table shows how closely the osmotic pressure calculated from the

[1] Wied. Ann., XXXI., p. 145.

[2] It is worthy of notice that the value 1.01831, obtained from Kahlenberg's freezing points for the ratio of the vapor pressures over pure water and over a sodium chloride solution of concentration 1, is confirmed by the direct and very careful observations of Dieterici (Wied. Ann., LXVII., p. 859). When Dieterici's observed ratios are plotted against the concentrations they determine a straight line which passes through the point (1, 0). From this line we find for the ratio above the value 1.0185. Not only so, but all of the ratios obtained for different concentrations from Kahlenberg's freezing points lie very accurately on the same line. The agreement of the results of these two sets of observations is a striking confirmation of the accuracy of both of them.

formula for various temperatures in the case of a solution of sodium chloride of concentration 1 agrees with those calculated by Gay-Lussac's law.

θ	273	293	313	333	353	373
P, formula	0.550	0.597	0.636	0.678	0.718	0.749
P, G. L. law	0.550	0.590	0.630	0.671	0.711	0.751

The agreement is very close in this case. As it depends on the relative values of the coefficients in the formula, it cannot be expected to be equally close in all cases.

If the formula for osmotic pressure is valid the temperature coefficient of the osmotic pressure becomes

$$\frac{1}{p}\frac{dp}{d\theta} = \frac{1}{\theta}\frac{p-l}{p}.$$

It becomes $1/\theta$ and the osmotic pressure conforms strictly to Gay-Lussac's law, when the temperature is that for which $l = 0$. For the sodium chloride solution of concentration 1, this coefficient equals 0.00438 at 0° C. and 0.00205 at 100° C.

5. *Origin of Osmotic Pressure.*—The first and last terms in the formula for the osmotic pressure are manifestly terms which do not depend upon the motions of the particles of the solute. They represent rates of change of energy with change of volume of the solution, and have been explained in my paper on "Heats of Dilution" by the assumption of forces acting between the molecules and ions of the solute and the molecules of the water. Their appearance in the formula for osmotic pressure indicates that the osmotic pressure arises from these forces and does not primarily depend upon the motions of the particles of the solute.

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ON CHARACTERISTIC ATOMIC CHARGES AND RESULTANT MOLECULAR CHARGES.

BY FERNANDO SANFORD.

IN a paper published a year ago under the caption "On Positive Atomic Charges"[1] I gave reasons for thinking that the positive sub-atoms of the elements have characteristic charges differing from each other and approximately proportional to the square roots of their atomic weights. On page 516 of that article I gave relative values for a few of these charges calculated in part from the velocity of ions in electrolysis and partly from data given by Richardson and Hulbirt in Phil. Mag., XX., 545, Oct., 1910.

In a paper "On Rays of Positive Electricity" in Phil. Mag., XX., 752, Oct., 1910, Sir J. J. Thomson gives values of e/m for a number of different positive particles found in the canal rays in an exhausted tube, and names these particles on the assumption that they carry positive charges equal to one or more unit hydrogen charges. In the paper referred to Thomson observed a number of fluorescent patches on his screen, one of which, a central patch called *o*, was not deflected by the electric or magnetic fields, while the others, named respectively *a*, *b*, *c*, *d*, *e* and *f*, showed deflection due to positive charges. The values of e/m calculated for the particles which produced these patches are given as follows: *a*, 65; *b*, 830; *c*, 2,900; *d*, 5,800; *e*, 11,600; *f*, 12,400. Thomson identifies these particles as follows: *a*, due to mercury vapor; *b*, due to atoms of oxygen or nitrogen; *c*, due to atoms of helium with one positive charge; *d*, due to hydrogen molecules with one surplus atomic charge; *e*, due to hydrogen atoms; *f*, due to secondary rays of some kind whose velocity is independent of the voltage in the tube.

In a paper by Professor C. T. Knipp on "Rays of Positive Electricity from the Wehnelt Cathode," Phil. Mag., XXII., 926, Dec., 1911, are given the values of e/m for a number of positive particles sent off from a hot platinum cathode on which is a spot of CaO. Knipp finds values of e/m which agree quite closely with those determined for canal rays from the anode by Sir J. J. Thomson.

Knipp's highest value of e/m is 9,400, and he identifies this with the hydrogen atom. His next value is $e/m = 4{,}960$, and this particle he

[1] PHYSICAL REVIEW, XXXII., 512, May, 1911.

identifies, after Thomson, as a hydrogen molecule with an excess positive charge equal to that on a single hydrogen atom. Thomson's values for the corresponding particles in the canal rays are 11,600 and 5,800.

Since it is difficult to see how a gas molecule could acquire an excess positive atomic charge without annexing the positive sub-atom which belongs with the charge, or could part with an electron without dissociating into atoms, it seems permissible to look for some other positive particle which may have the given value for e/m. Rutherford and Geiger found for the alpha-particle a value of e/m = 4,800 to 5,700, and since Knipp's value lies between these limits it seems at least as permissible to assume that there were alpha-particles in the tubes as to assume the existence of a gas molecule with an atomic charge.

In a paper entitled "The Significance of the Periodic Law," Journ. Am. Chem. Soc., XXXIII., 1349, Aug., 1911, I have given, as I believe, valid reasons for expecting alpha-particles to be given off from the anode in an exhausted tube. If such should prove to be the case, the tube should, in both investigations, contain particles having a value of e/m one half as great as the alpha-particle, and other particles which would not be deflected in the electric or magnetic field; for the alpha-particles would in both cases be compelled to traverse a region containing free electrons, and many of them, if not most of them, would take up one or two electrons in their flight. Those taking up one would have their value of e/m reduced by one half, and those taking up two would become electrically neutral helium molecules and be undeflected in the electric and magnetic fields.

Particles having one half the above value of e/m were numerous in Thomson's tube, but seem to have been rarer in Knipp's; but he gives several measurements on them with an average value of e/m = 2,380. Thomson identifies these particles as here indicated, viz., as helium atoms with one positive charge, which is the same as alpha-particles with one electron. The mean of Thomson's and Knipp's values of e/m for these particles is 2,640, while the mean of alpha-particles plus one electron should be from Rutherford and Geiger's determinations 2,625.

One spot on Knipp's plates which did not appear on Thomson's was due to particles having an average value of e/m = 1,700. This particle Knipp identifies as the carbon atom with two positive atomic charges. In a later paper in PHYSICAL REVIEW, XXXIV., 215, March, 1912, Knipp gives data on two plates made with a much higher accelerating field and a higher discharge potential, and finds spots produced by only two different kinds of particles, one with an average value of e/m = 4,830, which again is the correct value for the alpha-particle, and one giving

e/m = 1,860, and which he identifies as the one for which he determined the value 1,700 in his former plates. They are accordingly identified as carbon atoms carrying two positive charges, though in this case their value of e/m should equal one sixth that of the hydrogen atom, *i. e.*, 1,570 instead of 1,700, in the plates upon which both appeared.

Since the Wehnelt cathode was red hot in Knipp's experiments, it should have given off positive metallic ions of calcium and platinum. In my paper referred to above the relative values of the positive charges on hydrogen and calcium ions as calculated from their velocity in elec-

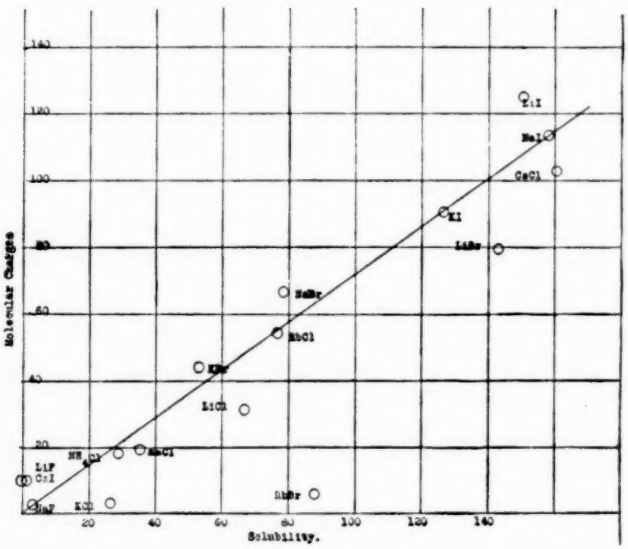

Fig. 1.

trolysis is as 11 to 79. Their relative values of e/m should accordingly be as 11 : 79/40 = 5.5 : 1, approximately. Using Knipp's value for hydrogen, e/m = 9,400, the value of e/m for calcium should accordingly be 1,700, as it was found to be in the same experiment. This seems to indicate that in the experiments described in the second paper Knipp found only alpha-particles and calcium ions in his tube.

In his first paper Knipp also gives the, so called, electric atomic weight of another set of particles, which varies from 21.7 to 23.2. Richardson and Hulbirt give for the electric atomic weight of platinum 25 and 25.7, respectively, for two sets of observations. Knipp does not name these particles.

In the curve plotted by me in the article referred to above[1] showing

[1] Also given in Plate I. of "A Physical Theory of Electrification," Leland Stanford Jr. Publications, University Series, No. 6, May 15, 1911.

the relation of the atomic charges as there calculated to the square roots of their atomic weights, it will be seen that the relative charge of platinum as calculated from Richardson and Hulbirt's data is apparently too large to correspond with its atomic weight. If the value of its electric atomic weight taken from Knipp's data be substituted, the relative charge of platinum in my table on p. 516 will be 431 instead of 474, which would be in much better agreement with the law there suggested.

If it be granted, as here suggested, that in Thomson's and Knipp's tubes were both alpha-particles and hydrogen atoms, it becomes a simple matter to calculate the absolute charges of the elements referred to in

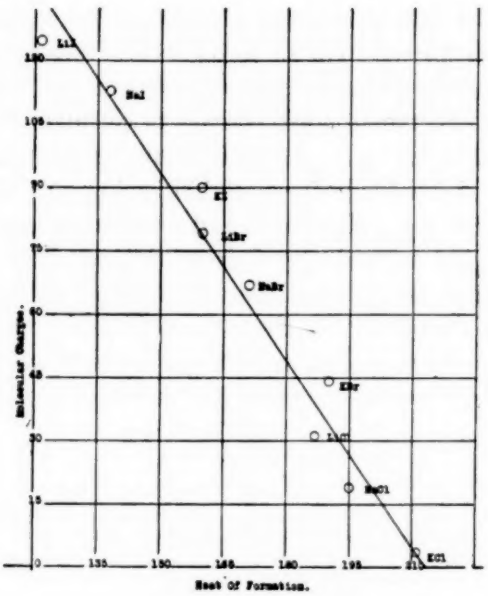

Fig. 2.

my former paper from the relative charges there given. Starting from the alpha-particle, which is the only gaseous ion whose charge has been directly measured, we can calculate the charge of the hydrogen ion from Thomson's and Knipp's data. Assuming the atomic weight of the alpha-particle as twice that of the hydrogen atom, its relative charge in my table would be 22 from Thomson's paper and 23.4 from Knipp's. Substituting its absolute charge for this value, the absolute charges of the other atoms are easily calculated.

While it is frankly admitted that the existence of these characteristic charges is still only a hypothesis, the same must be said of the assumption

that all positive ions carry simple multiples of the hydrogen charge. In the papers referred to above I have shown that these numbers calculated from the velocity of the ions in electrolysis are related to the atomic weight by the same laws as are a considerable number of other atomic constants which may reasonably be supposed to depend upon the electric condition of the atom. Among other properties, it was shown that the solubility of the monatomic gases in water is related to the square roots of the atomic weights as are the electric charges here assumed. It would seem to follow that other molecules should likewise be soluble in water in proportion to the difference between their molecular charges and the charge of the water molecules.

We are in a position to test this hypothesis in the case of some of the salts of the alkali metals and the halogen acids. If the molecules of these salts before dissociation in water were composed merely of the two ions which seem to take part in electrolysis, it is possible on the assumption of characteristic ionic charges to calculate the charge of the molecule before dissociation. In the following table these data are given for all the salts of this kind whose solubilities in water at zero are given in Seidell's Solubilities of Inorganic and Organic Substances, edition of 1907. The charges are calculated from the velocities of the ions in electrolysis, and are based upon the assumption that the charge of the hydrogen ion is 4.48×10^{-10}. They have all been multiplied by 10^{10}.

In the sixth column of the table is given the heat of formation of such of these compounds as are given in Julius Thomsen's Thermo-Chemistry.

Ion.	Charge.	Molecule.	Charge.	Solubility.	Heat of Formation.
F	− 13.6	LiF	− 9.6	.27	—
Cl	− 35.2	LiCl	− 31.	67.	187
Br	− 82.8	LiBr	− 79.	143.	160
I	−129.	LiI	−125.	151.	122
Li	+ 3.96	NaF	+ 2.	4.	—
Na	+ 15.8	NaCl	− 19.	35.6	195
K	+ 38.8	NaBr	− 67.	79.5	171
Rb	+ 89.	NaI	−113.	158.7	138
Cs	+138.	KCl	+ 3.6	27.1	211
NH_4	+ 17.7	KBr	− 44.	53.5	190
		KI	− 90.	127.5	160
		RbCl	+ 54.	77.	
		RbBr	+ 6.	89.6	
		CsCl	+103.	161.4	
		CsI	+ 9.	1.	
		NH_4Cl	− 17.5	29.4	

In order that the relation of the solubility and the heat of formation to these resultant molecular charges may be seen more clearly, two curves are given in which the resultant molecular charges are plotted against the solubilities and the heats of formation, respectively. While there are marked exceptions, of which RbBr is the most striking example, it will be seen that the solubilities are, at least roughly, proportional to the re will be seen that the solubilities are, at least roughly, proportional to the resultant molecular charges, and that the heats of formation are still more closely related to them.

Whatever explanation may be given for these relations, it seems unquestionable that what are here called resultant molecular charges are actual physical constants which are in some manner closely related to cohesion.

It, of course, follows from the above relations that the solubilities of these salts in water bear a definite relation to their heats of formation, as may be seen by plotting one of them against the other.

STANFORD UNIVERSITY,
June, 1912.

COMPARATIVE STUDIES OF MAGNETIC PHENOMENA. III.

MAGNETIC INDUCTION IN A GROUP OF OBLATE SPHEROIDS OF SOFT IRON.[1]

BY S. R. WILLIAMS.

IN the relation[2] between the Joule magnetostrictive effect and the magnetic induction in the same specimen of steel, I have pointed out that the maximum elongation of the steel rod in the Joule effect and the knee of the induction curve occur at the same magnetic field strengths. If the change in length of the steel rod is due to the orientation of elongated elementary magnets[3] then the orientation of these same elements, possessing the property of permeability, will produce in their turning changes in the magnetic induction. That is saying that the variation of B with H in the ordinary magnetization curve is not alone due to the intrinsic value of the permeability of the elementary magnets but is influenced by the orientation of those same elementary magnets. It is a well-known fact that an elongated piece of iron will turn so that its greatest length is parallel to the field imposed upon it. The converse of this must hold that if an elongated piece of iron is turned in the magnetic field, the magnetic flux will be changed in the piece of iron because a piece of ferro-magnetic substance sets itself in a magnetic field so that the magnetic resistance is a minimum.[4]

The occurrence of the maximum elongation and the knee of the induction curve at the same field strength emphasizes the point of view that there is some factor in the specimen of iron being investigated which simultaneously changes the length of the specimen and also varies the induction. This factor, I believe, is the elementary magnet. In this series of comparative studies on magnetic phenomena I have been trying to find some point of view that will unify our present knowledge of magetic phenomena and so far have found the idea of an elementary magnet, described in a previous paper, as being exceedingly helpful. No stress is laid on the theory only in so far as it leads to new facts.[5]

[1] Read by title at the Cambridge Meeting of the Amer. Phys. Soc., Apr., 1912.

[2] PHYS. REV., p. 258, Vol. 34, Apr., 1912.

[3] PHYS. REV., p. 40, Vol. 34, Jan., 1912.

[4] Starke, Experimentelle Elektricitatslehre, p. 75, 1904.

[5] Rücker, Pres. Address, B. A., Glascow, 1909. See Mellor, Higher Mathematics for Students of Chemistry and Physics, p. 365.

To give added support to the suggestions offered above, the magnetic induction in a group of oblate spheroids of soft Swedish iron was studied to see if their orientation produced an effect on the magnetic flux. Oblate spheroids were chosen as the form for the "elongated particles" because this was the shape ascribed to the nucleus of the model of the elementary magnet.

It is evident that if a definite number of these oblate spheroids were laid with the minor axes on the same straight line and touching each other that their total length would be less than though the same number were laid with major axes on a similar line. A change in length of such a group, due to their orientation, is obvious. The magnetic induction, however, may be considered at greater length and this paper has for its object the study of the magnetic induction in a group of twenty-seven oblate spheroids of soft Swedish iron, arranged in the form of a cube with nine spheroids on a side. The minor axes measured one centimeter and the major one and one half centimeters.

Miss Laura Anderegg, a graduate student in the department, carried out the measurements in the following way:

Miss Anderegg's Experiments.

The spheroids were laid up in the form of a cube as shown in Fig. 1 and paraffine poured in around them. This kept the spheroids in a definite position while testing the magnetic induction. This cube of spheroids was placed inside of a small secondary coil whose dimensions were, length 10.7 cm., cross-section 6.5 cm. square and the number of turns, 170. This coil was connected in series with a ballistic galvanometer and with its core of spheroids placed at the center of the large solenoid described in a former paper.[1] The induction was studied by the ordinary ballistic method employed in testing specimens of iron, steel, etc. As only relative values were wanted the deflections of the ballistic galvanometer were used to represent the total flux through the secondary.

Fig. 1.

In Fig. 2 is shown the relative values for the magnetic flux, (1) when the spheroids were removed from the secondary, (2) when the spheroids were in the secondary and the equatorial planes *normal* to the imposed magnetic field and (3) when the spheroids were in the secondary but the equatorial planes *parallel* to the field. In both curves 2 and 3 there was the same amount of ferromagnetic substance present but the orientation of the elementary units with respect to the field produced a comparatively

[1] Phys. Rev., p. 41, Vol. 34, Jan., 1912.

large change in the magnetic flux; when the major axes were *parallel* to the magnetic field the flux was greater than when the major axes were *normal*. For curves 2 and 3, Fig. 2, the spheroids were laid so that they touched each other in two directions at right angles, as shown

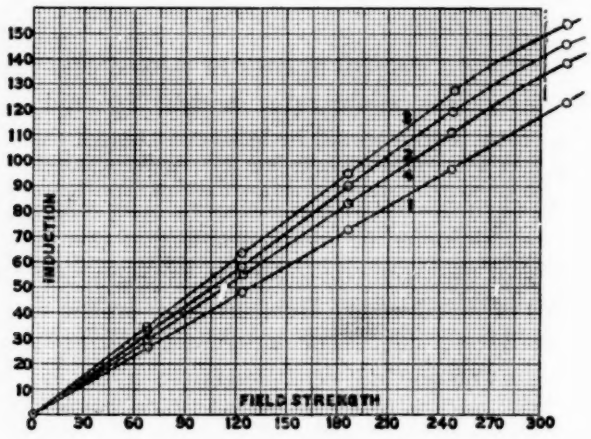

Fig. 2.

in Fig. 1. This made the length of the group shorter in one direction than in the other. When this shorter length was parallel to the imposed magnetic field there was less magnetic flux through the group than when the greater length was parallel. To make the outside dimensions of the group the same in all directions, the three layers shown in Fig. 1 were separated by strips of wood, as shown in Fig. 3. This was again tested when the equatorial planes were normal and when parallel to the field and the results are shown in curves 4 and 3 respectively. Curve 3 shows that the induction, parallel to the major axes, was the same as before the separation occurred, while 4 shows that a separation of the spheroids has decreased the magnetic flux in the direction in which the separation took place. This is an important result.

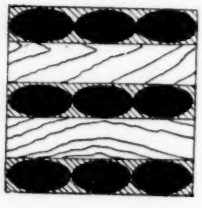

Fig. 3.

The spheroids were next set up so that their equatorial planes would make angles other than 0° and 90° with the imposed field. They were tested for 30°, 45° and 60° and the values fell between those of curves 2 and 3. The results seem to show that if one start with equatorial planes parallel to the imposed field that the magnetic flux decreases with the decrease of the diameter of the spheroids parallel to the field. The results of the experiments show that the magnetic flux in a group of spheroids may be influenced in two distinct ways: (1) by the orientation

of the spheroids and (2) by their separation. The flux is greater the more nearly the greatest length is parallel to the field and is decreased by increasing the distance between the surfaces of the spheroids.

Discussion of Results.

These results obtained by Miss Anderegg throw light on several magnetic phenomena with which we are familiar.

1. *Magnetization Curves.*[1]—In the magnetization curves of soft annealed iron and glass-hardened steel there is a very marked difference in the change of B with H in the two specimens. The knee of the curve occurs at smaller field strengths for soft iron than it does for the hardened steel. Hardened steel makes the best permanent magnets. This would indicate that the elementary magnets are not as free to turn in the hardened steel as in the soft iron. Consequently it will take a greater field strength to orient the elementary magnets a given amount in hardened steel than it does in soft iron. If a part of the increase of B therefore is due to the orientation of the elementary magnets, it must follow that the knee of the induction curve will not occur at as low field strengths for hardened steel as for soft iron, because it will take a larger magnetic field to bring the elementary magnets, which are producing the changes in length, so that their greatest length is parallel to the imposed field and it is at this point that the knee of the induction curve occurs. Previous work has shown that the maximum elongation of hardened steel in the Joule effect occurs at higher values of field strengths than it does in soft iron. If now the change in length may be ascribed to the orientation of the elementary magnets it would seem that we had here a most remarkable relation of phenomena.

2. *Application to the Villari*[2] *Reversal Effect.*—As is well known, certain steels when stretched in a weak magnetic field increase their magnetization but if stretched in a strong field lose in magnetization. In a weak magnetic field it is assumed that the elementary magnets are turned more or less in all directions with a tendency for those producing changes in length to turn with equatorial planes parallel to the field imposed upon them. This is shown in the change in length phenomenon. If a pull be applied to a steel rod in a weak field it helps to set the elementary magnets more nearly parallel to the field and so the magnetization is increased. On the other hand if a strong field is applied, *all* of the elementary magnets are turned with the equatorial planes normal to the field. Let a pull be applied to the rod in this last state when the magnetic

[1] Hadley, Mag. and Elec. for Students, p. 390.

[2] Villari, Pogg. Ann., 1868.

field has sufficient power to hold the elementary magnets fixed and the only thing that can occur is a separation of the elements. These experiments show that separating the spheroids decreases the magnetization. This is what occurs when a steel rod is stretched in a strong magnetic field.

3. *Application to Maurain's*[1] *Experiments.*—Maurain has pointed out that iron electrolytically deposited in a magnetic field shows anisotropic properties, *i. e.*, the elementary magnets seem to have been deposited with a definite orientation and therefore the intensity of magnetization has different values in different directions for the same field strength. Gans[2] has recently thrown doubt on the anisotropic property of iron but as Vallauri[3] has pointed out, Gans worked with too great a field strength (1,250 gauss). At such field strengths the elementary magnets are all turned in a definite direction and no matter in what direction such a field is applied to a specimen of iron it will force all of the elementary magnets with equatorial planes normal to the field. The group of spheroids used in these experiments is a model of the electrolytically deposited iron which shows different intensities of magnetization in different directions and the æolotropic property[4] of iron is a phenomenon which we should expect to find at proper field strengths.

In crystalline media such as pyrrhotine[5] we have a very pronounced case of a definite orientation of the elements in which we have different magnetic properties in different directions. It is only a step farther to assume that in the case of crystals showing rotation of the plane of polarization we have another manifestation of this same definite orientation of the elementary particles. This is being investigated in a series of crystals here in our laboratory.

SUMMARY.

1. The results of this investigation show that the orientation of the ellipsoidal elements does affect the magnetic flux. This furnishes a possible explanation as to why the maximum elongation and the knee of the induction curve come at about the same field strength.

2. The behavior of the ellipsoidal elements shows that not only orientation but also the distance between the bounding surfaces of the ellipsoids affect the magnetic properties.

3. This study also points out a possible explanation of the æolotropic properties of iron electrolytically deposited and why in other specimens

[1] Maurain, Phys. Zeitschr., 13, p. 314, 1912. Beetz, Pogg. Annal., CXL., p. 107, 1860.
[2] Gans, Phys. Zeitschr., 12, p. 911, 1911.
[3] Vallauri, Phys. Zeitschr., 13, p. 314, 1912.
[4] Klemencic, Phil. Mag., p. 424, Vol. 38, 1894.
[5] Weiss, Jour. de Phys., IV., pp. 469, 829.

of iron there appears to be no æolotropic properties at high field strengths.

4. I have attempted to show that because we have mechanical effects due to magnetization, such as we find in the magnetostrictive effects we must have some hypothesis of magnetization which will account for such phenomena. The ellipsoidal form of the elements, it seems to me, furnishes this part, as the elements are oriented under the influences of the forces operative upon them and produce changes in dimensions.

PHYSICAL LABORATORY,
OBERLIN COLLEGE, OBERLIN, OHIO.
March, 1912.

THE MAGNETIZATION OF HEUSLER ALLOYS AS A FUNCTION OF THE TEMPERATURE AND CALCULATION OF THE INTRINSIC MAGNETIC FIELD.

BY PERCY WILCOX GUMAER.

THE magnetic alloys of manganese are composed of metals which ordinarily are non-magnetic. Manganese itself is not only non-magnetic, but a small per cent of it will reduce the magnetic properties of iron. It is probable that the explanation of these magnetic alloys will add considerable to our understanding of the ultimate nature of magnetism.

Recent developments in the electron theory of magnetism have opened up a means of studying the molecular structure of the alloys.

The present investigation was undertaken with two objects in view, first: to study the effect of temperature upon the saturation value of the intensity of magnetization. Then, to determine, if possible, from the data obtained, the structure of the molecular magnets.

METHOD.

To determine the saturation value of the intensity of magnetization the method used by Weiss[1] and Stifler[2] was chosen. A ballistic galvanometer was connected in series with a helix placed in a strong magnetic field. An ellipsoid of the alloy to be tested was placed in the center of this helix and the deflection of the galvanometer was observed as the ellipsoid was, quickly, pushed out. The deflection of the galvanometer was then compared to that obtained from the current induced in the secondary of a standard helix which was included in the circuit. The intensity of magnetization I can be determined from the relation:

$$I = \frac{k}{v}\frac{i'}{d'}d,$$

where k = a constant depending upon the dimensions of the helix and of the standard helix.

v = the volume of the ellipsoid.

i = current in the primary of the standard helix.

d' = deflection due to induced current in the standard helix.

d = deflection when ellipsoid is removed from the helix.

[1] Archives des Sciences, ser. 4, 29, pp. 204 (1910).

[2] PHYS. REV., Vol. 33, p. 268 (1911).

The ellipsoid and helix were surrounded by a coil of German silver wire, by means of which the desired temperature was obtained. To measure the temperature of the ellipsoid inside the helix a copper-constantan thermo-couple was used. The hot junction was placed in a hard glass tube 3 mm. in diameter and 26 cm. long. Inside the tube the wires were separated by mica strips, outside by 1/16 rubber tubing.

The thermo-couple was calibrated by observing the E.M.F. of the couple when the hot junction was at a known temperature. The temperature of steam and the freezing points of metals were used for the calibration, as follows: Zn 419.4° C., Cd 321.0° C., Sn 231.9° C., steam 100° C. Using the method of least squares the constants of the equation $E = at + bt^2 + ct^3$ were determined and the equation becomes

$$E = 3.747t + .00375t^2 + .00000164t^3.$$

The galvanometer used was a Leeds & Northrup silver suspension instrument. It had a resistance of 25.6 ohms, a ballistic sensibility of 31.8 mm. per micro-coulomb on open circuit, with a scale distance of 50 cm., and a period of 11.2 seconds on open circuit. At a scale distance of 6 meters and the deflection could be read to 0.5 mm.

The ellipsoid was inserted directly into the tube forming the core of the helix. It was moved along by pushing with a small glass rod in one end and with the tube containing the thermo-couple in the other end. By this method the diameter of the helix could be decreased by half, which increased the sensitiveness considerably.

The induction helix was wound upon a thin-walled glass tube 45 cm. long and 0.5 cm. outside diameter. Three layers of number 36 silk-covered copper wire were used. The layers were separated by mica, and each layer was covered with a mixture of water glass and calcined magnesia. This mixture became very hard when dry and held the wires firmly in place even at high temperatures.

A hard glass tube long enough to reach to the end of the bore in the magnet was slipped over the helix coil. Thus the possibility of leakage from the heating circuit to the helix coil or lead-in wires was avoided. The heating coil consisted of one layer of 320 turns of number 16 German silver black enameled wire. The winding was done from the middle towards the ends so that the two halves were wound in opposite directions and opposed each other magnetically. As in the induction helix, a mixture of water glass and magnesia was used to hold the wires firmly in place. Since the length of the coil was 30 cm. the temperature gradient in the center was very small.

The induction helix and heating coil were enclosed in a glass tube small

enough to slide into the bore of the magnet. This tube was filled with calcined magnesia. Further heat insulation between the pole pieces was obtained by enclosing that part of the furnace in a fire clay cylinder filled with shredded asbestos.

The magnetic field was obtained from a large DuBois electromagnet. A hole drilled through the core and pole pieces enabled the ellipsoid to be inserted into the helix. For the air gap used (6.2 cm.) the strength of the magnetic field in the center of the gap was calibrated in terms of the current in the coils. A magnetic balance was used to measure the strength of the field.

DESCRIPTION OF SPECIMENS.

The alloys were prepared by melting in a new graphite crucible heated in a gas furnace. The manganese and copper were put in first, and when they were thoroughly fused the aluminum was added. To insure a uniform mixture, the molten alloy was stirred with a graphite rod, and then quickly poured into vertical moulds. Care was taken to pour in a continuous stream so that the oxide formed on the surface would not injure the casting.

The ellipsoids were obtained by grinding the castings with a properly shaped alundum wheel in a Universal Grinder. A projection of the shadow of the ellipsoids showed the cross-section to be fairly accurate.

The dimensions and composition of the two ellipsoids are given as follows:

	Ellipsoid No. 1.	Ellipsoid No. 2.
Length	1.686 cm.	1.680 cm.
Mean diameter	0.393 cm.	0.399 cm.
Volume	0.1364 cu. cm.	0.1401 cu. cm.
Mass	0.9487 gm.	1.0028 gm.
Density	6.96	7.15
Copper	62.9 per cent.	61.95 per cent.
Manganese	18.5 per cent.	21.9 per cent.
Aluminum	15.1 per cent.	15.9 per cent.
Undetermined	3.5 per cent.	0.25 per cent.

PROCEDURE IN TAKING READINGS.

After the heating current had been on for a time, sufficient to establish temperature equilibrium, the ellipsoid was inserted into the core of the helix. It was moved along by pushing with the tube containing the thermo-couple from one end and with a glass rod from the other end. A mark on the glass rod indicated when the ellipsoid was in the

center of the helix. When the temperature had ceased to increase the reading of the thermo-couple was taken, the magnetic field was thrown on and the deflection of the galvanometer was observed as the ellipsoid was quickly pushed out of the helix. A rapid movement of the ellipsoid was obtained by striking the end of the glass rod with a small piece of wood.

The ellipsoid was now replaced in position, allowed to regain its former temperature and the reading repeated. As a rule three readings were taken for each field strength and the intensity of magnetization was calculated from a mean of the three deflections.

At lower temperatures the deflections agreed to within 1 per cent. but in the neighborhood of the transformation temperature the agreement was not as close. For some of the readings taken above 300° the maximum deflection was 1 cm. at a scale distance of 6 meters. The accuracy in this case was probably about 10 per cent.

After each set of readings the galvanometer was calibrated by means of the standard helix. The current in the primary of the helix was read by a Weston milli-ammeter, which had been calibrated by comparison with a standard instrument. The ratio i'/d' varied slightly as the temperature increased, due to the increased resistance of the helix coil at higher temperatures. As the heating coil was wound non-magnetically, it was not necessary to make any correction for it.

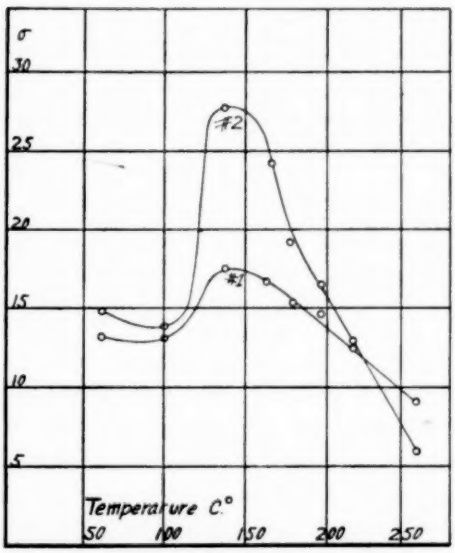

Fig. 1.

Thermo-couple readings were taken just before the ellipsoid was pushed out of the helix. As the end of the tube containing the thermo-couple was left open, and as the couple was within a millimeter of the end of the ellipsoid when readings were taken, it is quite probable that the temperature measured corresponded very accurately to the actual temperature of the ellipsoid.

Results.

The first set of data obtained is apparently of little theoretical value. The curves (Fig. 1) showing the specific intensity of magnetism σ as a

function of the temperature are quite irregular, having a maximum at 140°. Although it is possible that the irregularity of these curves is due to a defect in the apparatus, it is more probable that it is due to the unstable conditions of the alloys. The data were obtained with the alloys in the condition as cast and without previous heat treatment.

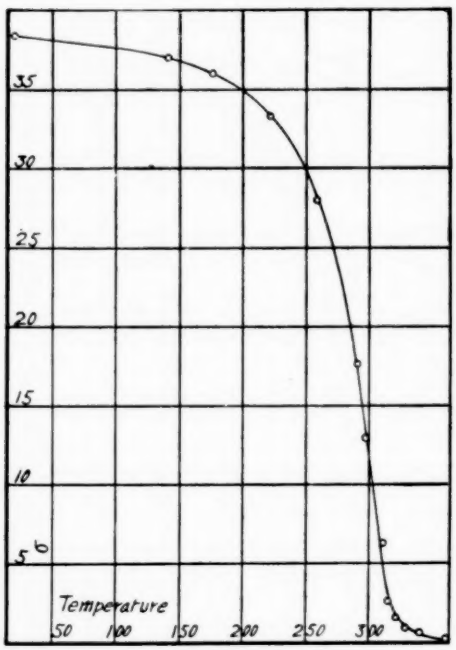

Fig. 2.
Ellipsoid No. 1.

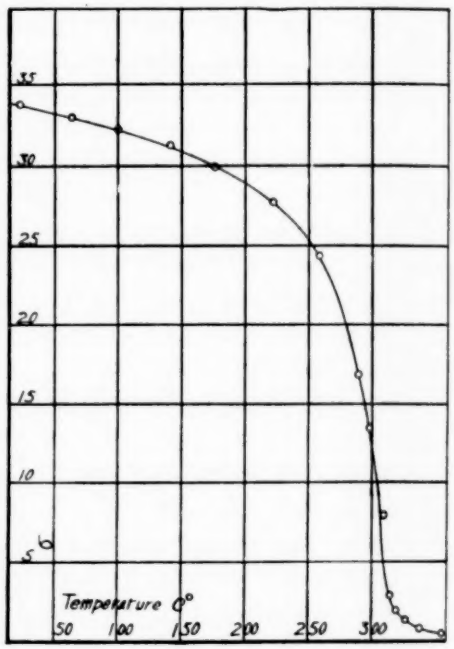

Fig. 3.
Ellipsoid No. 2.

A new helix coil was now built and a series of readings taken at 320° indicated that the substance had become paramagnetic. Beginning at room temperature, the whole set of data was repeated and very regular curves were obtained, as shown in Figs. 2 and 3. These curves, showing σ, the specific intensity of magnetization, as a function of the temperature, are similar to the ones obtained for iron, nickel and cobalt, although they are much flatter at lower temperatures. It is seen from the curves that the temperature of transformation is in the neighborhood of 310°. A theoretical discussion of these curves will be given in a later paragraph.

As the values of σ at room temperature were found to be about half of what should be expected from the theoretical calculations, an attempt was made to increase the magnetic intensity by chilling from a temperature near the melting point of the alloy. To do this the ellipsoids were inserted in a quartz tube together with a platinum platinum-rhodium

thermo-couple, and heated in an electric furnace to 895° C. They were kept at the temperature for 10 minutes and then chilled by plunging the quartz tube into cold water.

The value of the intensity of magnetization was found to have been increased considerably by the chilling. Values of σ were obtained, as before, for different values of temperature below the transformation point. The curves are shown in Fig. 4.

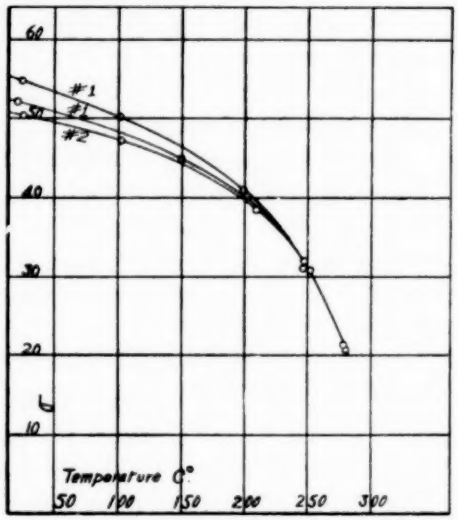

Fig. 4.

In order to be sure of the results the chilling was repeated for ellipsoid No. 1 and similar values were obtained.

The following table shows a typical set of readings taken at 290° C. The value of σ at each field strength was obtained from the mean of three galvanometer deflections. The temperature was obtained from the mean of the thermo-couple readings. These were not allowed to vary more than 20 micro-volts, which corresponds to 0.4°.

mv	d	Mean d	σ	I	LI	I_m	H_0	H
13,670	27.5							
13,680	27.3	27.4	15.9	114.0	85	2.0	930	845
13,675	27.5							
13,670	27.8							
13,680	27.7	27.7	16.1	115.3	86	3.0	1,395	1,309
13,670	27.7							
13,675	29.0							
13,665	28.8	29.0	16.8	120.5	90	4.0	1,860	1,750
13,665	29.2							
13,670	29.0							
13,670	28.7	28.9	16.75	120.0	90	5.0	2,335	2,245
13,675	29.0							
13,670	29.0							
13,670	28.8	28.9	16.75	120.0	90	6.0	2,730	2,640
13,665	28.9							

TYPICAL SET OF DATA. TAKEN AT 290.9°.

Ellipsoid No. 2.

$I = 4.157d, \quad \sigma = 0.580d, \quad L = 0.749.$

d = deflection of the galvanometer,
mv = reading of thermo-couple in microvolts,
I_m = current through the magnet,
H_0 = external field,
H = field inside the ellipsoid = $H_0 - LI$,
I = intensity of magnetization,
σ = specific intensity of magnetization.
Mean value of thermo-couple readings = 13,670 m.v.
Corresponding temperature = 290.9°.
Deflection due to standard helix = 70.3.
Current in primary of standard helix = 0.672 ampere.

MOLECULAR THEORY OF MAGNETISM.

The present theory of magnetism, as developed by Curie,[1] Weiss,[2] Langevin[3] and Kunz,[4] accounts for the various phenomena by assuming that a magnetic substance is made of small elementary magnets.

In a non-magnetic state these elementary magnets are distributed with their axes pointing equally in all directions. Under the influence of a resultant magnetic field H, each elementary magnet is acted upon by a turning force $MH \sin \alpha$, where M is the moment of the elementary magnet and α is the angle between H and the axis of the magnet. The tendency of this couple is to cause the magnets to turn with their axes toward the direction of the existing field. The amount of this rotation depends upon the strength of the field and upon the temperature of the substance.

If there were no thermal agitation of the molecules all the elementary magnets would revolve until their axes coincided with the direction of the existing field. This condition is obtained at absolute zero.

At other temperatures than absolute zero the magnetic energy of the molecules tending to arrange the molecules in the direction of the magnetic field is opposed by the thermal energy. The molecules are continually being deflected by their mutual collisions, and the resultant condition of equilibrium depends upon the ratio of the thermal energy to the magnetic energy.

[1] Archives des Sciences, ser. 4, 31, p. 5–19 (1911).
[2] Journal de Physique, 36, p. 661–690 (1907).
[3] Annales de Chemie et de Physique, Ser. 5, 8, p. 70–127 (1905).
[4] PHYS. REV., 30, p. 359–370 (1910).

Consider a sphere of unit radius within which are a large number of magnetic molecules. When there is no magnetic field acting, the magnets are distributed with their axes pointing equally in all directions. Imagine all these magnets concentrated with their centers at o. Under the action of a magnetic field the magnets will be caused to rotate about o, and the tendency will be to place their axes in line with the magnetic field. The magnets will no longer have their axes pointing uniformly in all directions, but the magnetic density will be greatest in the direction of H. Let us define magnetic density as the number of magnetic axes per unit solid angle or $dn/d\omega$. For abbreviation put $\rho = dn/d\omega$.

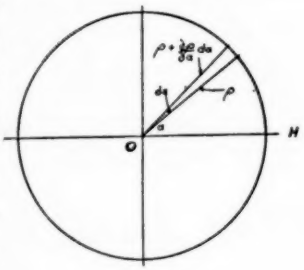

Fig. 5.

Let ρ be the magnetic density at any angle α with the field H. Then at angle $\alpha + d\alpha$ the magnetic density will be $\rho + (\partial\rho/\partial\alpha)d\alpha$. The change of magnetic density in moving through angle $d\alpha$ is therefore

$$\rho - \left(\rho + \frac{\partial\rho}{\partial\alpha}d\alpha\right) = -\frac{\partial\rho}{\partial\alpha}d\alpha.$$

This change of density depends upon the density ρ at α. It is also proportional to a resultant turning force or couple.

If we assume that the molecules of iron, or other ferro-magnetic substance, when in a non-magnetic state are as free to move relatively to each other as the molecules of a gas, then the thermal energy can be deduced from the laws of thermo-dynamics. Since a rotation of the elementary magnet about its own axis has no effect upon its magnetic energy, there remain but two degrees of rotation. Hence, for the molecular magnets, the kinetic energy of heat is equal to RT, where R is the universal gas constant and T is the absolute temperature.

In dynamics work/angle = a couple, hence $RT/d\alpha$ = a couple due to the thermal energy of the molecules. The magnetic couple acting upon the elementary magnets is $MH \sin \alpha$.

The change of magnetic density varies directly as the magnetic couple and inversely as the couple due to the heat energy; that is, the greater the magnetic couple, the greater will be the change of magnetic density as we pass from α to $\alpha + d\alpha$, and the greater the thermal energy, the smaller will be the change of density. Hence we can put

$$-\frac{\partial\rho}{\partial\alpha}d\alpha = \rho\frac{MH\sin\alpha}{\frac{RT}{d\alpha}} = \rho\frac{MH\sin\alpha\cdot d\alpha}{RT}.$$

Then

$$-\frac{\partial \rho}{\partial \alpha} = \rho \frac{MH}{RT} \sin \alpha;$$

and

$$-\frac{\partial \rho}{\rho} = \frac{MH}{RT} \sin \alpha d\alpha.$$

Integrating

$$\log \rho = \frac{MH}{RT} \cos \alpha - \log K;$$

whence,

$$\rho = K e^{\frac{MH}{RT} \cos \alpha},$$

or

$$\frac{dn}{d\omega} = K e^{\frac{MH}{RT} \cos \alpha}.$$

But

$$d\omega = 2\pi \sin \alpha d\alpha;$$

hence

$$dn = K e^{\frac{MH}{RT} \cos \alpha} 2\pi \sin \alpha d\alpha. \qquad (1)$$

Intensity of magnetization may be defined as the product of the number of molecular magnets per unit volume and the moment of the magnets in the direction of the resultant magnetic field. The intensity is a maximum when there is no thermal agitation, so that the molecular magnets are all directed along the field. This condition obtains only at absolute zero.

At other temperatures the intensity due to the magnets whose axes make an angle α with H is

$$dI = M \cos \alpha dn,$$

where M is the moment of the molecular magnets, and I is the intensity of magnetization.

Substituting the value of dn from eq. (1), we have

$$dI = M \cos K e^{\frac{MH}{RT} \cos \alpha} 2\pi \sin \alpha d\alpha;$$

and integrating between limits 0 and π

$$I = \int_0^{\pi} M \cos \alpha K e^{\frac{MH}{RT} \cos \alpha} 2\pi \sin \alpha d\alpha.$$

Now let

$$\frac{MH}{RT} = a, \quad \cos \alpha = x, \quad -\sin \alpha d\alpha = dx;$$

then,

$$I = 2\pi MK \int_{+1}^{-1} xe^{ax}dx.$$

But

$$\int_{+1}^{-1} xe^{ax}dx = \frac{a(e^a + e^{-a})}{a^2} - \frac{(e^a - e^{-a})}{a^2}$$

$$= 2\left(\frac{\cosh a}{a} - \frac{\sinh a}{a^2}\right);$$

hence

$$I = 2\pi MK2\left(\frac{\cosh a}{a} - \frac{\sinh a}{a^2}\right). \tag{2}$$

To evaluate K, integrate equation (1):

$$n = 2\pi K \int_0^{\pi} e^{a\cos\alpha} \sin\alpha d\alpha$$

$$= \frac{4\pi K}{a} \sinh a;$$

whence

$$K = \frac{na}{4\pi \sinh a}.$$

Substituting the value of K in equation (2), we have

$$I = 2.2\pi M \frac{na}{4\pi \sinh a}\left(\frac{\cosh a}{a} - \frac{\sinh a}{a^2}\right)$$

$$= Mn\left(\frac{\cosh a}{\sinh a} - \frac{1}{a}\right).$$

But $Mn = I_m$; hence,

$$I = I_m\left(\frac{\cosh a}{\sinh a} - \frac{1}{a}\right), \tag{3}$$

where

$$a = \frac{MH}{RT}. \tag{4}$$

Equations (3) and (4) give us an expression for the intensity of magnetization as a function of the temperature.

So far we have considered only the arrangement of the elementary magnets due to the action of an external field. Each magnet, however, has an effect upon the surrounding magnets and the result according to the Weiss theory is a uniform field, proportional to the intensity of magnetization, I, and acting in the same direction as I. This molecular magnetic field accounts for the great magnetic intensity of iron and

other ferro-magnetic substances in the same way as an internal pressure added to the external pressure accounts for the great density of liquids. The sudden increase of density when a vapor liquefies is due to the fact that an enormous internal pressure is suddenly made effective in addition to the external pressure. Ferro-magnetic substances at high temperatures are but slightly magnetic. As the temperature is slowly decreased a point is reached at which the substances suddenly become very magnetic. This indicates that a strong molecular field has become operative. If H_m represents the molecular field and I the intensity of magnetization then $H_m = AI$ where A[1] is a proportionality factor.

The resultant magnetic field within the substance is, consequently, the sum of the external field, H_e and the molecular field H_m, or, $H = H_e + H_m$.

From equation (4)

$$T = \frac{MH}{aR};$$

whence

$$T = \frac{M(H_e + H_m)}{aR}. \tag{5}$$

The large magnetic intensity of ferro-magnetic substances at ordinary temperatures indicates that the molecular field must be very strong in comparison with the external field. This condition holds up to the temperature at which the substance ceases to be ferro-magnetic. Let θ be that temperature, then for $T = \theta$, we can neglect H_e in comparison to H_m and equation (5) becomes

$$T = \frac{MAI}{aR}, \quad \text{for } T \leqq \theta. \tag{5a}$$

From equation (3)

$$I = I_m\left(\frac{\cosh a}{\sinh a} - \frac{1}{a}\right).$$

The expression $\left(\frac{\cosh a}{\sinh a} - \frac{1}{a}\right)$ can be expanded into the convergent series

$$\frac{1}{3}a - \frac{2}{90}a^3 + \frac{4}{45\cdot 42}a^5 \cdots.$$

For very small values of a it is sufficient to consider only the first term of the series, and equation (3) becomes

$$I = \frac{aI_m}{3}. \tag{6}$$

[1] In order to avoid ambiguity later the symbol A is chosen in preference to N, the symbol used by Weiss, Kunz and others.

For $T = \theta$ equation (5) may be written

$$\theta = \frac{MAI_m}{3R}. \tag{7}$$

Dividing equation (5) by (7), we have

$$\frac{T}{\theta} = \frac{\frac{M(H_e + AI)}{aR}}{\frac{MAI_m}{3R}} = \frac{3H_e}{aAI_m} + \frac{3}{a}\frac{I}{I_m}.$$

But

$$I = \frac{a}{3} I_m;$$

hence

$$\frac{T}{\theta} = \frac{H_e}{AI} + 1.$$

Solving for A, we have

$$A = \frac{H_e}{I}\frac{\theta}{T - \theta}. \tag{8}$$

Knowing A, we can calculate H_m, the strength of the molecular field, since $H_m = AI$.

We can also calculate M, the moment of the elementary magnet, for from equation (7) we have

$$\theta = \frac{MAI_m}{3R},$$

or

$$M = \frac{3R\theta}{AI_m}. \tag{9}$$

Discussion of Results.

The curves (2) and (3), showing σ as a function of the temperature indicate that the temperatures at which the alloys cease to be ferromagnetic is in the neighborhood of 310° C.

Knowing θ it is possible to express T as a function of the parameter a. Then by comparing the graph obtained with the experimental curve near the transformation point, we can calculate a value for I_m, the intensity of magnetization at absolute zero.

Equation (5a) can be written in the form

$$I = \frac{aRT}{MA}.$$

Dividing through by I_m, we have

$$\frac{I}{I_m} = \frac{R}{MAI_m} aT.$$

But from equation (7)

$$\frac{R}{MAI_m} = \frac{1}{3\theta};$$

hence

$$\frac{I}{I_m} = \frac{1}{3\theta} aT,$$

and

$$T = \frac{3\theta}{a}\frac{I}{I_m} = \frac{3\theta}{a}\left(\frac{\cosh a}{\sinh a} - \frac{1}{a}\right). \qquad (12)$$

Putting $\theta = 310° + 273° = 583°$ and evaluating equation (12), we obtain the following values:

a	$\frac{\cosh a}{\sinh a}$	$\frac{\sigma}{\sigma_m} = \frac{\cosh a}{\sinh a} - \frac{1}{a}$	T	t	$74.5\frac{\sigma}{\sigma_m}$
0.3	3.4328	0.0995	580	307	7.0
0.4	2.6317	0.1317	577	304	9.8
0.5	2.1639	0.1639	574	301	12.2
0.6	1.8619	0.1952	569	296	14.5
0.8	1.5059	0.2559	560	287	19.1
1.0	1.3131	0.3131	548	275	23.3
1.2	1.1995	0.3662	534	261	27.3
1.6	1.0849	0.4599	503	230	34.3
2.0	1.0373	0.5373	470	197	39.9
3.0	1.0049	0.6716	392	119	50.0
4.0	1.0007	0.7507	328	55	55.9
5.0	1.0000	0.8000	280	7	59.6

Since

$$\frac{I}{I_m} = \frac{\sigma}{\sigma_m},$$

$$\sigma_m = \frac{\sigma}{\frac{\cosh a}{\sinh a} - \frac{1}{a}},$$

where σ_m is the value of σ at absolute zero.

In the following table the experimental values of σ are compared with the calculated values of σ/σ_m for values of t above 250°.

t	σ Observed.	σ/σ_m Calculated.	Value of σ_m.
297.7	12.9	.184	70.1
297.7	13.5	.184	73.4
290.9	17.6	.234	75.5
290.9	16.8	.234	71.8
258.9	28.5	.372	76.6
			74.5 mean

It is evident that if we divide the observed values of σ by the calculated values of σ/σ_m we can determine the value of σ_m. Taking the mean of several values, we get $\sigma_m = 74.5$. If we now multiply the values of $\frac{\cosh a}{\sinh a} - \frac{1}{a}$ by 74.5, we obtain corresponding values for σ and t. Using these values we can plot a theoretical curve for σ and the temperature. Such a curve is shown in Fig. 6.

It will be noticed that the experimental values of σ as given by the dotted lines agree with the theoretical values for high temperatures, but at low temperatures the experimental curve bends away from the other. The same phenomenon is observed in iron, nickel and cobalt, but to a lesser degree. In the case of the magnetic alloys the bending is less (curve B) after the alloy has been chilled from a high temperature.

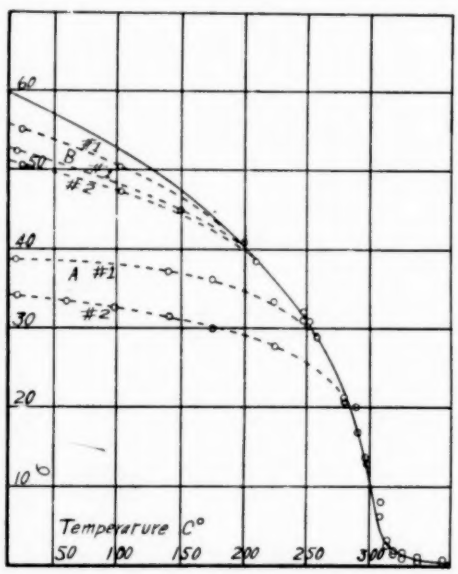

Fig. 6.

Since the internal or molecular field becomes negligible above the transformation temperature, the intensity of magnetization becomes proportional to the external field, and from a knowledge of the magnetic properties of the alloy in its paramagnetic state we calculate H_m the intrinsic molecular field and m the moment of the elementary magnets.

In doing this we will first calculate A, the proportionality constant.

From equation (8) we have

$$A = \frac{H_e}{I} \frac{\theta}{T - \theta},$$

where H_e is the external field and I is the intensity of magnetization at temperature T.

Calculations of A are given in the following table for various values of T. They give for ellipsoid No. 1 $A = 12{,}940$; for ellipsoid No. 2 $A = 10{,}540$.

Ellipsoid No. 1.

Temp. = 314.5°.			Temp. = 320°.		
H_e	I	$K = I/H_e$	H_e	I	K
462	3.93	.00851	465	1.98	.00427
924	7.42	.00803	927	4.02	.00434
1,382	14.4	.01041	1,390	6.23	.00448
1,844	17.9	.00973	1,853	7.56	.00408
2,319	18.2	.00788	2,326	10.25	.00440
Mean .00891		A = 14,560	Mean .00439		A = 13,270
Temp. = 327.7°.			Temp. = 340°.		
H_e	I	K	H_e	I	K
464	1.31	.00282	1,394	1.79	.001284
928	2.62	.00282	2,726	4.15	.001521
1,392	3.92	.00282	3,425	5.68	.001658
1,855	5.23	.00282	3,695	7.0	.001894
2,329	6.54	.00281			
Mean .00282		A = 11,700	Mean .00159		A = 12,230

Ellipsoid No. 2.

Temp. = 314.5°.			Temp. = 320°.		
H_e	I	$K = I/H_e$	H_e	I	K
463	4.61	.00996	463	2.26	.00489
923	9.66	.01046	926	5.83	.00630
1,384	15.14	.01094	1,389	7.96	.00573
1,846	18.92	.01026	1,852	10.83	.00584
			2,326	12.00	.00518
Mean .01040		A = 12,460	Mean .00559		A = 10,430
Temp. = 340°.			Temp. = 360°.		
H_e	I	K	H_e	I	K
1,393	2.74	.001966	1,394	1.904	.001365
2,726	5.77	.002115	2,728	3.38	.001240
3,425	6.74	.001967	3,427	4.23	.001233
3,825	7.37	.001926	3,827	4.02	.001050
Mean .001993		A = 9,760	Mean .001227		A = 9,500

Ellipsoid No. 1.		Ellipsoid No. 2.	
Temp.	A	Temp.	A
314.5	14,560	314.5	12,460
320.0	13,270	320.0	10,430
327.7	11,700	340.0	9,760
340.0	12,230	360.0	9,500
Mean A = 12,940		Mean A = 10,540	

The calculation of the other quantities consists merely in substituting in the equations already obtained. The work is summarized as follows:

		Ellipsoid No. 1.	Ellipsoid No. 2.
σ_m,		74.5	74.5
d = density,		6.96	7.15
$I_m = d\sigma_m$,		518	533
$A = \frac{He}{I}\frac{\theta}{T-\theta}$,	(8)	12,940	10,540
$H_m = AI_m$,		6,700,000	5,620,000
$M = \frac{3R^1\theta}{AI_m}$,	(9)	$3.55 \cdot 10^{-20}$	$4.23 \cdot 10^{-20}$
$N = \frac{I_m}{M}$.	(10)	$1.46 \cdot 10^{22}$	$1.26 \cdot 10^{22}$

$$R = 1.36 \cdot 10^{-16}.$$

For comparison, the constants obtained for iron and nickel by Kunz[2] and for cobalt by Stifler[3] are given in the following table:

	I_m	θ	A	H_m	$M \times 10^{-20}$.	$N \times 10^{22}$.
Iron.....	2,120	756° C.	3,850	6,560,000	5.15	4.12
Cobalt.....	1,435	1,075	6,180	8,870,000	6.21	2.31
Nickel	570	376	12,700	6,350,000	3.65	1.56
Alloy No. 1.	518	310	12,940	6,700,000	3.55	1.46
Alloy No. 2.	533	310	10,540	5,620,000	4.23	1.26

If we assume that there is one atom of manganese in the magnetic molecule then for alloy number one we have the relation

$$m_H = \frac{d}{wn},$$

where m_H = weight of a hydrogen atom.

$w = 55$ = atomic weight of manganese.

$n = 1.46 \cdot 10^{22}$ the number of magnetic molecules per cu. cm.

d = density of alloy × per cent. of manganese in alloy.

$= 6.96 \cdot 0.185$.

$$m_H = \frac{6.96 \cdot 0.185}{55 \cdot 1.46} 10^{22} = 1.60 \cdot 10^{-24}.$$

[1] R is the universal gas constant, and the value to be used is that corresponding to one molecule.

[2] PHYS. REV., Vol. 30, p. 259 (1910).

[3] PHYS. REV., Vol. 33, p. 268 (1911).

This value of m_H agrees almost exactly with $1.61 \cdot 10^{-24}$, the value obtained by Rutherford. From alloy number two we get $m_H = 2.12 \cdot 10^{-24}$, which does not agree very closely.

If e is the elementary charge of the hydrogen atom and α_H is the chemical equivalent of hydrogen, then $e = m_H/\alpha_H$. Using the values of m_H obtained above we get from alloy number one $e = 1.54 \cdot 10^{-20}$ and from alloy number two $e = 2.04 \cdot 10^{-20}$.

We could have obtained, however, the same values by assuming that the magnetic molecule was composed of one atom of manganese and one atom of aluminium, or one atom of manganese and one atom of copper. Since a molecule must contain more than one atom, it is quite probable that the magnetic molecule is a composite molecule containing one atom of mangenese and one atom either of copper or of aluminium. This hypothesis would also account for the increase in the intensity of magnetism after chilling from a high temperature, as shown in Fig. 6. The chilling prevents one of the metals from crystallizing out and thus prevents a decrease in the number of molecular magnets.

The author hopes to continue the investigation and to determine definitely the number and kind of atoms in the elementary magnet, and also to study the effect of the percentage of copper upon the transformation temperature. These results will be important in proving that the magnetic properties are due to the manganese.

SUMMARY.

The chief results of this investigation may be summarized as follows:

1. The temperature of magnetic transformation from the ferromagnetic to the paramagnetic state was established at 310° C. for the alloys containing 62 per cent. copper.

2. The curve giving σ as a function of the temperature has been shown to agree with the theoretical curve above 200°.

3. Chilling from near the melting point causes the experimental curve to follow the theoretical curve to a lower temperature than before.

4. The nature of the molecular field was found to be of the same order of magnitude as nickel, all the constants I_m, H_m, M and H, being of approximately the same value.

5. The results, while not extensive enough to determine the number and kind of atoms in the elementary magnet, are sufficient to show that the alloys obey the laws of ferro-magnetism, as derived by the present molecular theory.

6. The fundamental equation (1), on which the present theory of

magnetism is based, has been derived mathematically; thereby, making the former analogy to the gas theory unnecessary.

The writer takes pleasure in acknowledging his indebtedness to Professor Jakob Kunz for his general supervision of the work, and for many valuable suggestions.

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April 25, 1912.

NOTES ON OPTICAL CONSTANTS OF METALS.

BY J. T. LITTLETON, JR.

INTRODUCTION.

THIS work consists in the determination of the values of the optical constants, that is, n the refractive index and k the absorptive index, for silicon and ductile tungsten, and a study of the effect of heat treatments on different steels. Observations have been made on silicon and tungsten by von Wartenberg[1] and on silicon by Ingersoll and Littleton.[2] The specimens used in this investigation are much purer than the one used by von Wartenberg, and, in addition to observations (by another method), on the same piece studied by Ingersoll and Littleton measurements are made on a piece with a different crystalline structure, and on one showing the Hall and thermo-electric effects in a direction different from the others. The metallic tungsten used in this work is of an entirely different form from the one used by von Wartenberg.

Many observers have measured the optical constants of steel, but with no concordance of results. This lack of agreement among different experimenters must be largely due to the fact that measurements were made on specimens of entirely different carbon content and having no similarity as regards heat treatment.

Hagen and Rubens[3] give the values of 55.4 per cent. for the reflecting power of soft steel and of 60.0 per cent. for hard steel for light of a wavelength of 6,000$\mu\mu$ and Drude[4] using sodium light gives for steel the value 58.5 per cent., but in neither case is the carbon content specified or is the heat treatment prescribed other than merely by the words hard and soft. But it is well known that these two factors have a great influence on all of the physical properties of the metal. It is therefore of interest to see whether the optical properties are so affected, and whether by this means the apparent disagreement between different experimenters can be explained.

EXPERIMENTAL METHOD.

Since the method used for the determination of the values of n and k is that used by Drude,[5] no experimental details need be given.

[1] D. Phys. Gesell. Verh., 12, p. 105, 1910.

[2] PHYS. REV., 31, Nov., 1910.

[3] Zeits. f. Instrumentk., 22, 52, 1902.

[4] Ann. Phys., 39, 481, 1890.

[5] Ann. Phys., 39, 481, 1890.

All grinding was done with graded carborundum, and the polishing with rouge on a pitch tool or with rouge on broad-cloth. But since this latter method has a tendency to give a relief polish it is not desirable in all cases.

As a source of light fused sodium chloride in a blast lamp was used for the measurements on silicon and tungsten, but the Meker burner with a platinum holder for the sodium chloride used for the steels proved much more satisfactory.

Observations were made at principal incidence and principal azimuth, that is, at that angle of incidence, at which light plane polarized at an angle of 45° with the plane of incidence, becomes circularly polarized after reflection from the metallic surface. Angles of incidence could be read to 30″ and azimuth to 0.1°.

If $\bar{\phi}$ be the angle of principal incidence and $\bar{\psi}$ the principal azimuth the well-known Drude formulæ become for this position:

$$n = \sin \bar{\phi} \tan \bar{\phi} \cos 2\bar{\psi} + \frac{\cos \bar{\phi} \cos 2\bar{\psi}}{2},$$

$$k = \tan 2\bar{\psi}(1 - \cot^2 \bar{\phi}).$$

The reflecting power is calculated from n and k by:

$$R = \frac{n^2(1 + k^2) + 1 - 2n}{n^2(1 + k^2) + 1 + 2n}.$$

I. Silicon.

Observations were taken on four pieces of silicon obtained from the Carborundum Co., of Rochester, N. Y., having a purity of 99.75 per cent. No. 1 had a good black polish, though not free from scratches, No. 2 was from the same plate as No. 1, and was scratched in only one direction with carborundum which had remained suspended in water for five minutes, No. 3 was the flat surface of a crystal and No. 4 was a piece giving thermo-electric effects and Hall effects in a direction opposite to the others. Since these give the same values for n and k to within the possible experimental error, results will be given for the first piece only, this having the best polish of the four. This is also the same plate on which measurements out in the infra-red to 2.5μ were made by Ingersoll,[1] and by Ingersoll and Littleton[2] by another method.

The means of ten observations at angles of incidence equal to 68°, 70°, 72°, 74°, and 76° give:

[1] Astr. Phy. Jour., Vol. XXXII., p. 265, 1910.

[2] Phys. Rev., Vol. XXXI., p. 489, 1910.

$n = 4.24$, $k = 0.118$, $\bar{\phi} = 76° 45'$, $2\bar{\psi} = 6° 52'$, $R = 37.8$ per cent

The greatest deviation from the mean was 1.5 per cent. for n and 7 per cent. for k, $\bar{\phi}$ and $2\bar{\psi}$ were calculated and the above value of R is the calculated reflecting power. R measured by a Martens-Koenig spectrophotometer is 37.7 per cent. This result is accurate to 0.5 per cent. The reflecting power for the Rest-strahlen from quartz of 9μ wave-length was measured by means of a Rubens thermopile and was found to be 33.5 per cent.

Von Wartenberg using silicon 95 per cent. pure and light of a wave-length $5.790\mu\mu$ gets:

$n = 3.87$, $k = 0.116$, $\bar{\phi} = 75° 38'$, $2\bar{\psi} = 7° 3'$, $R = 35.7$ per cent.

This difference between the two determinations is readily explained by the difference in purity.

II. TUNGSTEN.

A thin plate of ductile tungsten having the dimensions 1.5 by 0.5 square centimeters was obtained from the General Electric Co. Scratches did not have much effect on either principal incidence or principal azimuth, but the final observations were on a surface practically free from scratches.

The means of ten sets of measurements of $\bar{\phi}$ and $2\bar{\psi}$ gave:

$n = 3.46$, $k = 0.94$, $\bar{\phi} = 78° 31'$, $2\bar{\psi} = 44° 3'$, $R = 54.5$ per cent.

Von Wartenberg using a form of pressed tungsten and light of a wave-length equal to $5,790\mu\mu$ gets the following results:

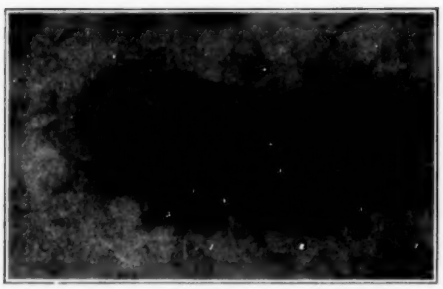
$n = 2.76$, $K = 0.98$, $\bar{\phi} = 76° 0'$, $2\bar{\psi} = 46° 20'$, $R = 48.6$ per cent.

This difference is no doubt due to the different form of metal used.

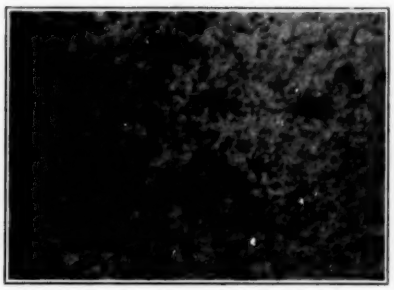
III. THE EFFECT OF HEAT TREATMENTS AND CARBON CONTENT ON THE OPTICAL PROPERTIES OF STEEL.

Measurements were made on five surfaces of 0.44 per cent. carbon steel, on five of 1.28 per cent. carbon steel, on one of about 3.5 per cent. carbon and one of pure iron. These steels were obtained from Prof. E. D. Campbell of the department of chemistry and are of accurately known composition and heat treatment.

Steels may be divided into four classes, the basis of division being the crystalline structure as controlled by heat treatments. CLASS I. is a mixture of the segregated particles of the carbides of iron in a matrix of pure iron, and is obtained by holding the metal at a temperature of about 600° C. for twenty-four hours or longer, which treatment allows the carbides of iron to collect into large particles. CLASS II. is very similar, differing only in degree, the particles of the iron carbides being very small.



No. 1D.
High power.



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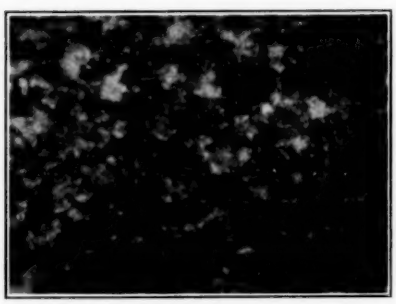
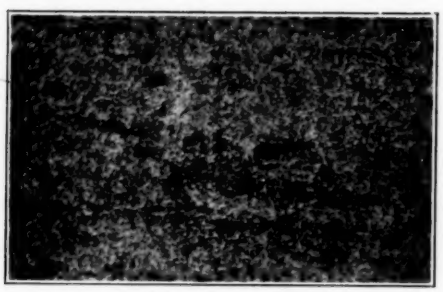


No 5D.
High power.



No. 5D.
Low power.

This structure is obtained by slow annealing from about 900° C. or by quenching from 900° C. and reheating to about 600° C. and holding at this temperature for eight or ten hours. The carbides begin to go out of solution and to collect into very fine particles. This form of steel is called perlite. CLASS III. is, according to Campbell,[1] a supersaturated solution of the carbides of iron in α iron. This structure is obtained by quenching from about 900° C. and reheating to about 340° C. and holding at this temperature for ten or more hours. This structure is called troostitic. In opposition to Campbell's view is the theory that this steel consists of very finely divided particles of the carbides of iron mechanically mixed in the iron crystal. CLASS IV. is the quenched or hardened steel and is obtained by holding the specimen at a temperature around 900° C. for thirty minutes and quenching in ice water. This gives a solid solution of the carbides of iron in small γ iron crystals.

These treatments cause quite a difference between the two extremes of structure, that is, between the segregated iron and the quenched and hardened. The micro-photographs of the 1.28 per cent. carbon steel show this characteristic difference. In the segregated iron the segregated particles are clearly shown under the low power magnification and one large particle is shown under the high power. The difference between the two structures is clearly visible. Microscopic examination of the surfaces prepared from the other specimens showed them to be good examples of their class.

After microscopic examination the etching was ground off and the surface repolished and the observations taken. The means of ten observations on these surfaces are given in the following table.

Optical Constants of Steel.

No.	Per Cent. C.	Φ	2Ψ	n	k	R
No. 1*C*	0.44	77° 10′	53° 55′	2.59	1.30	57.2
No. 2*C*	0.44	77° 11′	53° 55′	2.59	1.30	57.2
No. 3*C*	0.44	77° 18′	53° 55′	2.61	1.30	57.5
No. 4*C*	0.44	77° 16′	53° 55′	2.61	1.30	57.5
No. 5*C*	0.44	77° 18′	53° 55′	2.61	1.30	57.5
No. 1*D*	1.28	77° 16′	53° 30′	2.63	1.28	57.4
No. 2*D*	1.28	77° 26′	53° 30′	2.67	1.28	57.4
No. 3*D*	1.28	77° 12′	53° 30′	2.63	1.28	57.6
No. 4*D*	1.28	77° 30′	53° 30′	2.68	1.28	57.5
No. 5*D*	1.28	77° 28′	53° 30′	2.68	1.28	57.5
No. 1*E*	3.5	77° 35′	52° 24′	2.77	1.23	57.0
No. 1*F*	0.00	77° 1′	54° 10′	2.53	1.31	56.2
Drude	Steel	77° 8′	55° 38′	2.41	1.41	58.5
Drude	Iron	76° 30′	54° 58′	2.36	1.36	56.2

[1] Jour. of Iron and Steel Inst., p. 318, 1908.

Assuming a correct polish these results are correct to the second decimal figure.

No. 1*C* was annealed for sixteen hours from 900° C. and is a segregated piece. No. 2*C* was quenched from 900° C., reheated to 600° C. and held at this temperature for twelve hours. No. 3*C* was quenched from 900° C. and reheated to 340° C. and held at this point for twelve hours. No 4*C* was quenched from 900° C., reheated to 200° C. and held at this temperature for eighteen hours. This reheating does not affect the structure to a noticeable degree, yet it softens the steel sufficiently to allow cutting. No. 5*C* was held at 1000° C. for thirty minutes and then quenched. No. 1*D* was held at 600° C. for twenty-four hours No. 2*D* was quenched and reannealed, the exact time and temperatures not being known. Microscopic examination showed that it belonged more to class III. than to class II. No. 3*D* was cooled from 1000° C. to 200° C. during sixteen hours. This is a good specimen of perlite. No. 4*D* was quenched from 900° C. and heated to 340° C. No. 5*D* was held at 950° C. for thirty minutes and quenched in ice water.

Nos. 1*C* and 1*D* belong to class I. Nos. 2*C* and 3*D* to class II., Nos. 3*C*, 2*D* and 4*D* to class III., Nos. 4*C*, 5*C* and 5*D* to class IV.

Drude's[1] results are given for comparison.

Discussion of Results.

It is seen that the results of Drude differ from those given here and that the difference is much larger than the error of observation. The difference lies mainly in the values obtained for principal azimuth, and this value is affected by scratches and not so much by the purity of the surface. Impurity of the surface, that is, a surface film, tends to decrease the value of principal incidence, and these results do not indicate any such impurity, the principal incidence in all cases being larger than that of Drude. From previous work[2] by the author on the optical constants of iron and nickel alloys the curve plotted between n and the per cent. of iron intersects the iron axis at a value of n equal to 2.48, and the curve between k and the per cent. of iron could be drawn to the iron axis at a point giving the value for k of 1.31. This leads to the conclusion that the iron observed by Drude contained some other metal, or else that there is some constant error in the method of polishing used here. But if for any reason these values of n are too high and of k too low they are consistently so, and the difference between the different steels exists independent of the absolute values of the optical constants.

[1] Ann. der Phys., 39, 481, 1890.

[2] Phys. Rev., 33, p. 453, 1911.

The fact that classes I. and II. give the same values for n and k proves that the light reflected from the large particles of the carbides of iron combines with that from the pure iron and gives light of the same form as is obtained from the small particles and the pure iron. Since this proves that the size of the particles up to this extent has no effect and since classes III. and IV. have the same values for n (and this value is different from that of classes I. and II.) the conclusion is that the carbides of iron have some effect on the iron molecule in both the hard steel and the troostitic form. This furnishes good evidence in support of the theory held by Campbell mentioned previously.

The decrease in k caused by an addition of carbon is so small that a change caused by heat treatment cannot be observed. But the changes in n caused by changes in carbon content and by heat treatments are quite large. Hence lack of similarity in these two factors could easily account for any lack of agreement between measurements of the optical constants of steels of unknown compositions and heat treatments.

In conclusion the author wishes to express his thanks to Prof. C. E. Mendenhall, of the University of Wisconsin, for assistance in the first part of this work, to Prof. E. D. Campbell, of the department of chemistry of this university, for suggestions and for specimens used in the work on steel, to Mr. A. E. White for assistance on the micro-photographs, and to Prof. K. E. Guthe for the apparatus used and for his interest in the progress of the work.

PHYSICAL LABORATORY, UNIVERSITY OF MICHIGAN,
June, 1912.

THE KERR ROTATION FOR TRANSVERSE MAGNETIC FIELDS, AND THE EXPERIMENTAL VERIFICATION OF WIND'S MAGNETO-OPTIC THEORY.[1]

BY L. R. INGERSOLL.

Introduction.—There may be distinguished three different types of phenomena—collectively referred to as the "Kerr effect," although Kerr himself was able to observe only the first two—which arise when a surface of iron, nickel, or cobalt, on which is incident plane polarized light, is magnetized. The three types correspond to the three possible cases of magnetization, viz., with the lines of force normal to the reflecting surface, or lying in the surface and respectively parallel or perpendicular to the plane of incidence of the light. The phenomena in general are somewhat complicated inasmuch as they are superposed on the optical effects which accompany the reflection of light from the unmagnetized surface. In the simplest and best known case—the reflection at normal incidence from a surface at which the lines of force are also perpendicular—the effect of magnetization is practically nothing but a simple rotation of the plane of polarization; in other cases the phase change and accompanying ellipticity, which is very weak in this simple case, become prominent. While a number of experimenters have made measurements for the first two types, the third case, *i. e.*, where the magnetic lines of force are normal to the plane of incidence—the so-called "equatorial" magnetization[2]—has, because of the minuteness of the effect, heretofore escaped observation with the exception of a single determination for iron made by Zeeman.[3]

The writer was led to take up the present work by a brief study of the effects of magnetization on the optical constants of the magnetic metals. The method which had been developed and used for determining optical constants, particularly in the infra-red spectrum,[4] was found to be capable of such accuracy that it would seem to be possible as well as desirable to study the effect of various directions of magnetization on the azimuth of the reflected light. It was soon realized, however, that while observations of such azimuth changes were easily obtained they were in general

[1] This and the correlated work has been materially aided by grants from the Rumford Fund of the American Academy of Arts and Sciences.

[2] See Voigt, "Magneto- und Electrooptik, p. 277.

[3] Arch. Neer. (II)., 1, p. 221 (1898).

[4] Astrophys. Jour., 32, p. 265 (1910).

difficult to interpret, for the problem under these conditions became the complicated one of the Kerr effect for oblique incidence. For the case of transverse or "equatorial" magnetization, however, the results were found to be of peculiar interest because of the closeness with which they followed the predictions made by the late C. H. Wind[1] in his magneto-optic theory, and it is this experimental work which will be described.

Wind's Theory.—This explanation of the Kerr effect shares with those of other physicists of the Leyden school many of the characteristics of the Lorentz theory, in particular the idea of a new vibration component introduced by the magnetic field. Its interest from our standpoint lies in the completeness with which its author has worked out the case of magnetization perpendicular to the plane of incidence. He concludes that this should give rise to a minute difference of phase in the two component vibrations and to a small change in azimuth, this effect being due to the change in the component of the polarized light whose electric vector lies in the plane of incidence, *i. e.*, normal to the lines of force. The other component will not be altered. The effects which should be expected in the case of each of the three magnetic metals, for the wave-length of sodium light, have been worked out in detail, and the curves for the azimuth change—the phase change cannot be experimentally considered in this paper—are reproduced in Fig. 1. The azimuth change is not

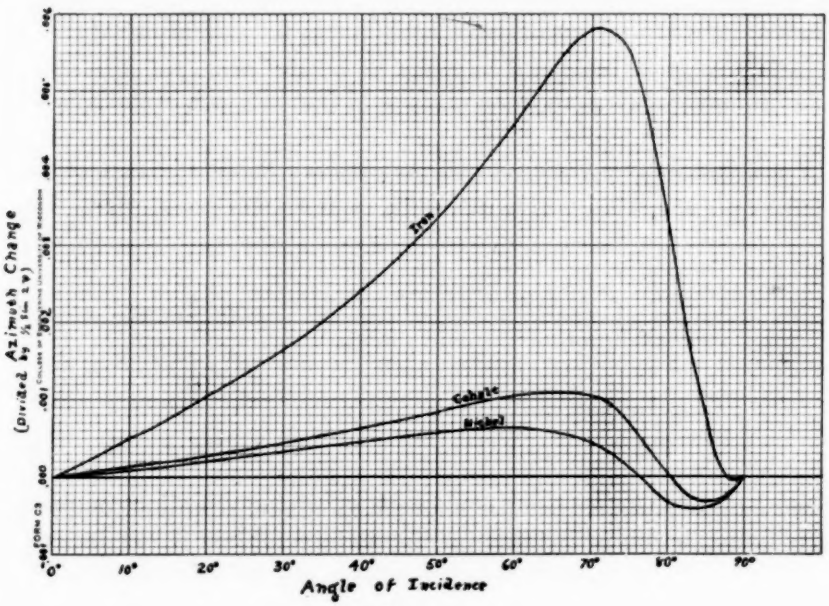


Fig. 1.

Wind's theoretical curves for azimuth change with transverse magnetization.

[1] Arch. Neer. (II.), 1, p. 119 (1898).

directly expressed in these curves, but rather a quantity which is this change, measured in fractions of a radian, divided by $\frac{1}{2} \sin 2\psi$, where ψ is the "azimuth of restored plane polarization."

At the time of the appearance of Wind's theory no one had been able to detect an effect of this sort, but shortly afterward Zeeman succeeded in making observations in substantial agreement with the predictions of the theory both as regards azimuth and phase change, for the case which should yield a maximum effect, viz., iron at 75° incidence. So far as the writer is aware the subject has not been further handled experimentally up to the present time.

The present experiment may be outlined briefly as follows: Light from a Nernst glower (*G*, Fig. 2) is plane polarized and reflected from the surface (*S*) under trial. It will then in general be reduced to an elliptically polarized vibration, of which the two components are taken by passage through a large double image prism "analyzer" (*A*). The intensity of these two components can be compared for any wave-length by a special spectrobolometric apparatus.[1]

While the ratio of these two components would enable one to find at once the "azimuth of restored plane polarization"—if this state of polarization is imagined restored by a suitable phase change—it is found much more convenient in practice to keep the two components of the same intensity by changing the azimuth of the incident polarized light. This azimuth of restored polarization—the *principal azimuth* if the corresponding angle of incidence happens to be the *principal incidence*—is then read off at once as the (complement of the) azimuth of the polarizing agent.

A comparison of this method with the ordinary Babinet scheme of determining optical constants is worth while to make this point clear. Fig. 3

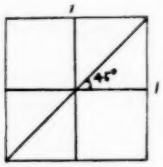


Fig. 3.

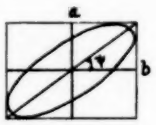


Fig. 4.

shows a plane polarized beam of azimuth 45° giving vibration components each unity, which is incident on the surface. Then if the factors by which the two amplitudes are changed are respectively a and b, Fig. 4 represents the vibration after reflection, the phase change being such

[1] For details of this arrangement see Astrophys. Jour., 32, p. 265 (1910).

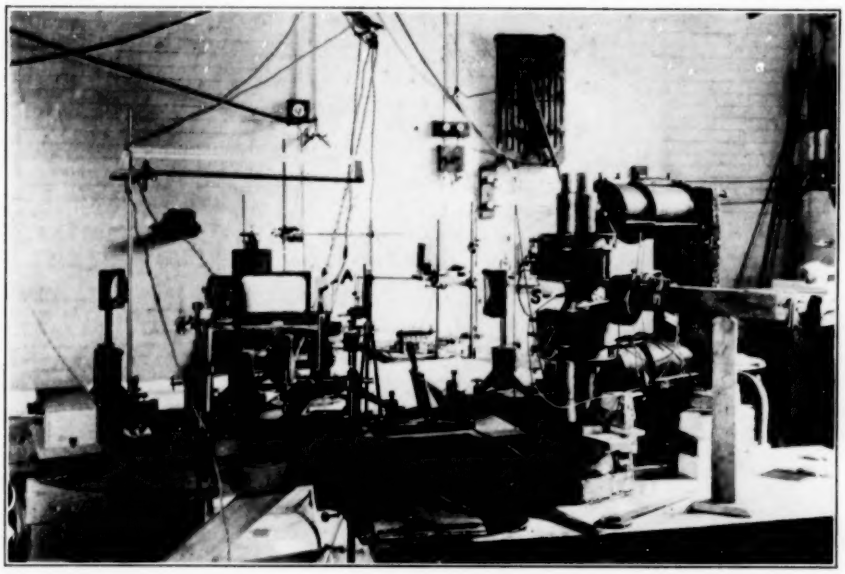


Fig. 2.
L. R. INGERSOLL

in general as to render it elliptical. If this elliptical vibration is then reduced by the Babinet compensator to plane polarized light the azimuth would be given by $\psi = \tan^{-1} b/a$. In the present method the component vibrations are equal after reflection (Fig. 6) and this evidently necessi-

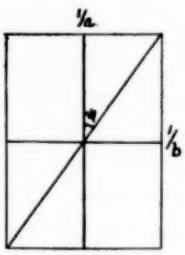


Fig. 5.

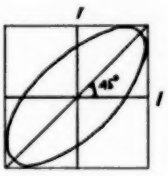


Fig. 6.

tates original components proportional to $1/a$ and $1/b$, so that the azimuth of the polarizer must be $90 - \psi$.

The magnetic field is produced by a powerful electromagnet, between whose poles the surface is held in a specially devised clamp. When the magnet is excited the azimuth ψ is changed to ψ^1 and the polarizer must be turned to azimuth $90 - \psi^1$ to make the two components equal again. The difference $\delta\psi$ is the change due to magnetization and is the quantity with which we are concerned. While it would also be of interest to measure the change of phase which accompanies this azimuth change, this would involve a complicated modification of the method which has not as yet been attempted, and which does not, at best, appear promising.

The procedure in making observations is slightly different from that indicated above but almost equally simple. As the change of azimuth on magnetization is a very small quantity—usually only a few minutes of arc—the galvanometer deflection corresponding to such change is determined as accurately as possible by repeated reversals of the magnet current. The deflection caused by a measured change of azimuth (*i. e.*, rotation) of the polarizer of, say, 15 minutes of arc is then noted, and the magnetic effect deduced by a simple proportionality. A correction is of course necessary for any direct action the magnet may have on the galvanometer.

Accuracy of the Measurements.—It will be readily understood that in work of this character—many of the angles of rotation are too small for even detection by the Babinet—a high degree of accuracy is not to be expected. Generally speaking the sources of error[1] are those incidental

[1] See papers by the writer in Phil. Mag. (6), 11, p. 51 (1906); PHYS. REV., 23, p. 489 (1906); Phil. Mag. (6), 18, p. 86 (1909); Astrophys. Jour., 32, p. 274 (1910).

to the writer's spectrobolometric method of studying polarization phenomena, but the chief source of error in the present case lay in the discrepancy which was frequently found between measurements made for the two azimuths lying symmetrically on each side of the normal. This was apparently due to a small component of the magnetic field perpendicular to the metal surface and hence could be eliminated by merely averaging the two results. This was done for the best observations, such as those for sodium light, and it is probable that the error in these measurements does not exceed a very few per cent.

Results.

Two distinct series of observations were made with somewhat different experimental arrangements. In the first case parallel light was incident on the test surface while in the second the light converged to an image

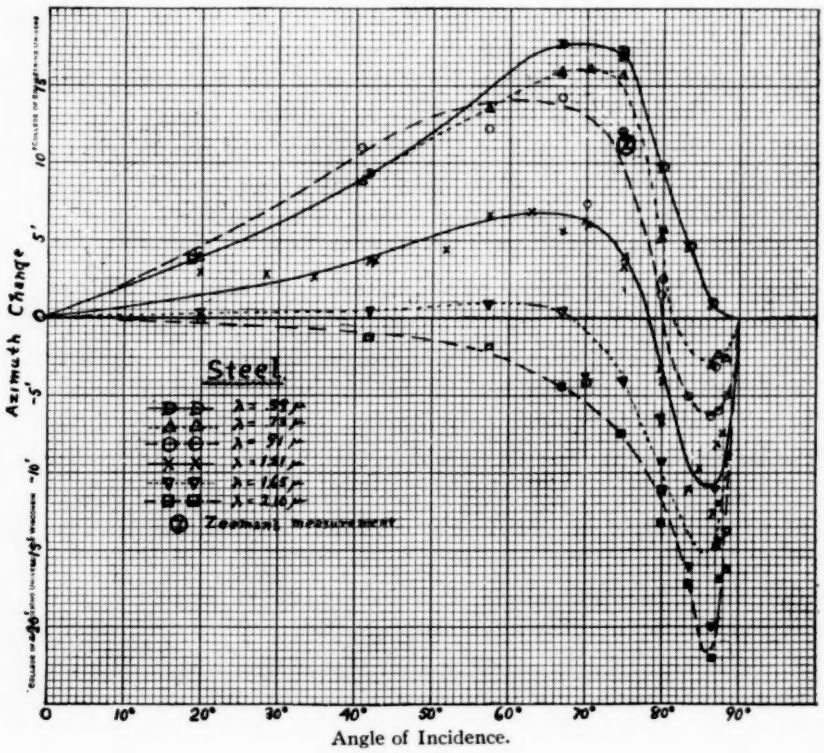


Fig. 7.

Azimuth curves for steel.

of the Nernst glower at this surface. The results were in substantial agreement. While the first method was theoretically preferable as giving a perfectly definite angle of incidence, the second had the decided ad-

vantage of affording much more light, especially for very oblique angles of incidence and as the extreme variation of incidence was hardly 3° the uncertainty from this source of error was not a serious objection and did not exceed a degree. The mirrors of steel, nickel, and cobalt were 5 cm. in diameter and about 5 mm. thick. They were optically plane and very perfectly polished, having been finished by Zeiss. Steel was used rather than iron because it takes a better polish. Its optical characteristics are very nearly the same as those of iron,—so much so that we shall not distinguish between them.

Measurements in the Visible Spectrum.—The observations were at first confined to about the same range of wave-length as that for which it had been found possible to measure the dispersion of these metals, viz., 0.8μ to 2.2μ; but later it was found that when every precaution was taken to save light from losses at the various reflections, and to secure freedom from vibrations and other disturbances, it was possible to make very good observations even into the visible spectrum. These were carried out for the wave-length of sodium light (because of the low dispersion and wide slit necessary, the light really varied in wave-length from about 0.56μ to 0.62μ) and were particularly valuable as affording a direct check on Wind's predictions, as these were based on observations made only for this wave-length.

A general survey of the results may be obtained from Figs. 7 to 9, where practically all the determinations have been plotted as a function of the angle of incidence and for a number of wave-lengths. A positive azimuth change means that the azimuth is increased by the magnetic field under the following conditions: the lines of force running from left to right, as the observer sees the surface looking obliquely down on it in the direction in which the light is travelling. The values plotted are the doubled effects due to reversals of the magnet current.

While the consistency of the observations is not all that could be desired in many cases there is no chance for question as to the general form of the curves, viz., a zero value of the azimuth change for normal and for grazing incidence, and in general a positive maximum followed by a negative maximum for very oblique incidence. The general effect of an increase in wave-length is clearly to decrease the positive part and increase the negative part of the curve. By making measurements on the separate components it was found moreover that the only one affected was that vibrating in the plane of incidence or normal to the field, as predicted by theory.

For a more careful analysis of the results and a comparison with theory we shall consider only the measurements for the wave-length of sodium

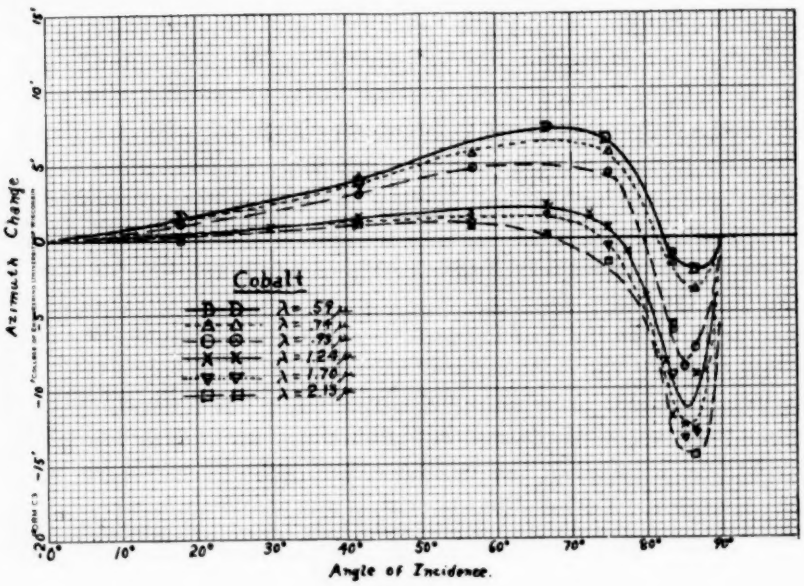


Fig. 8.

Curves for cobalt.

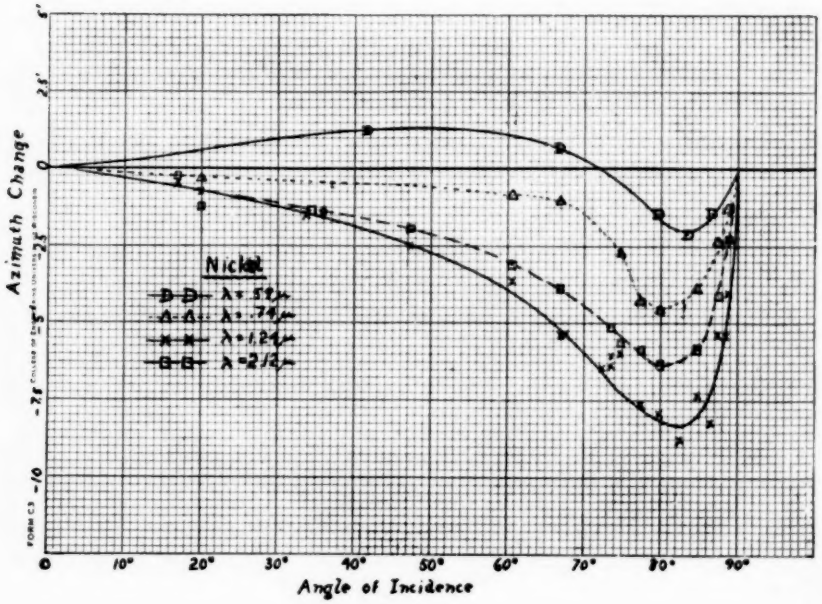
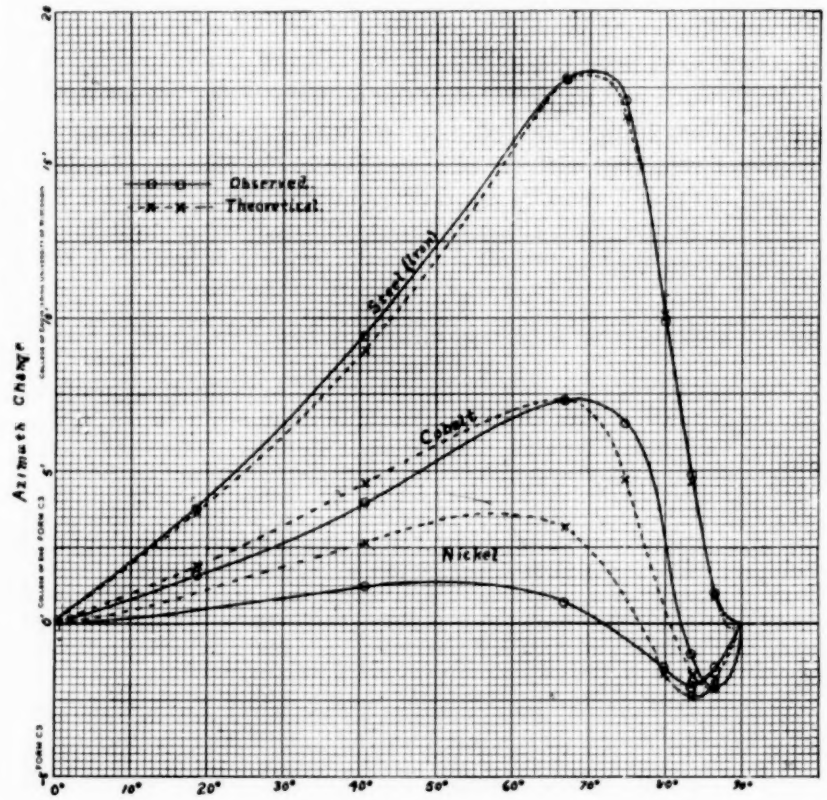


Fig. 9.

Curves for nickel.

light. A comparison of the curves of Fig. 1 with the corresponding ones in Figs. 7 to 9 shows at once the qualitative agreement of the results with Wind's theory, but for a more careful examination they must first be reduced to the same scale.

To do this Wind's results are first changed from circular measure to minutes of arc and then multiplied by the factor $\frac{1}{2} \sin 2\psi$. The angle ψ is readily computed for any angle of incidence from the equations given by



Angle of Incidence.

Fig. 10.

Theoretical and observed curves for the azimuth change accompanying transverse (equatorial) magnetization, for the wave-length of sodium light.

Drude (Optik, p. 344), Drude's values of the optical constants being used in this connection. The results (Wind's) are then doubled since our measurements are for reversal of the magnetic field.

The theoretical results would then be ready for comparison with the observations if they were computed for the same intensity of magnetization. This, however, is not quite the case. Wind's calculations for

iron are based on observations made for an intensity of magnetization of 1,400, while in the present case the induction was found by measurement to be 25,000 lines, which for this particular specimen—about .8 per cent. carbon—means an intensity of magnetization of perhaps 1,500. For cobalt the measured induction of 14,000 would mean an intensity two or three times that of Wind's which was only 430. For nickel the induction rather than the intensity was specified, and was given as 8,000 lines, while that in the present case was about 14,000.

To reach an exact basis of comparison, then, Wind's results for iron and cobalt have been multiplied by the ratio of the intensities—more exactly by such factors as to bring the maxima of the curves together, the multipliers being 1.07 and 2.08 for iron and cobalt respectively—and plotted, together with the observed results, in Fig. 10. In the case of nickel, although there is smaller theoretical justification for it, the ratio of the inductions has been used as a factor. The following table summarizes the results:

TABLE I.

Comparison of the Theoretical and Observed Values of the Azimuth Change for the Wave-length of Sodium Light.

Incidence.	Steel (or Iron).		Cobalt.		Nickel.	
	Theoretical.	Observed.	Theoretical.	Observed.	Theoretical.	Obs.
18.6°	3.67′	3.77′	1.93′	1.60′	——	——
40.8	8.98	9.42	4.62	3.98	2.68′	1.24′
66.9	17.80	17.80	7.30	7.30	3.18	0.70
74.6	16.57	17.11	4.73	6.56	——	——
79.9	10.08	9.87	——	——	−1.62	−1.41
83.4	4.70	4.88	−1.71	−1.00	−2.36	−2.09
86.4	0.88	1.00	−2.08	−2.07	−1.76	−1.40

For steel and cobalt the agreement between the predictions of this theory and the results of experiment must, under the circumstances, be considered as very good. In the case of nickel the agreement is only qualitative, making perhaps another instance in which this metal exhibits optical characteristics distinct from the other two magnetic metals.[1]

Experiments with Heusler's Alloy.—Over half a dozen years ago the writer[2] found that the Kerr effect (normal incidence and normal magnetization) was apparently absent in the Heusler alloy, despite its other magnetic properties. As this result has been rather widely quoted and was, moreover, based on experiments with the earlier and cruder forms of the writer's apparatus, it seemed worth while to try Heusler's metal

[1] Phil. Mag. (6), 11, p. 72 (1906).

[2] Ibid.

in connection with the present work. The piece selected was a different specimen from that formerly used and was very strongly magnetic. The results are given in the accompanying table, and also the approximate azimuth changes for steel under the same conditions.

TABLE II.

Wave-length.	Incidence.	Azimuth Changes.	
		Heusler Alloy.	Steel.
.93μ	40.8°	0.005′	10.2′
1.24	66.9	−0.015′	6.8′
1.70	84.4	0.003′	−15′

Similar measurements for normal (or polar) magnetization and an incidence of about 30° gave a possible rotation for this same specimen of alloy not to exceed one or two tenths of a minute. We may then safely conclude that magneto-optic effects of this sort, if they exist at all in Heusler's metal, are less than a hundredth as large as the corresponding effects in steel.

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UNIVERSITY OF WISCONSIN,
July, 1912.

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